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C O N T E N T S

Kinetic Regularities of the Reactions of Hydrazides of Organophosphorus Acids with Phenylisothiocyanate

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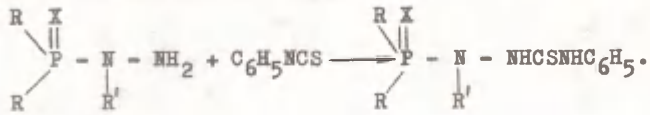
On the basis of kinetic studiee of the reactions of organophosphorus hydrazine compounds with phenylisothiocyanate possible mechanism of these reactions and also causes of the manifestation of α-effect in them are discussed. α-effect is shown to be dependent to a very large extent on the structure of the transition state.

In the reactions with phenylisocyanate hydrazides of organophosphorus acids have the increased reactivity which is due to α-effect [1,2]. Assuming that α-effect is to a very large extent determined by the structure of the transition state [3,4], the increase in the reactivity of the hydrazine organophosphorus compounds can be accounted for by their ability to form a five-membered cyclic complex in the transition state owing to the hydrogen bond between the hydrogen atom of the hydrazide imino group and oxygen or isothionate nitrogen atom [1,2].

The purpose of the present work is to verify this assumption. It is dealing with kinetic studies of regularities of the reactions of hydrazides and α-ethylhydrazides of diphenylphosphinic, O,O-diphenylphosphoric, and O,O-diphenylthiophosphoric acids with phenylisothiocyanate in benzene, i.e. reactions where the formation of the cyclic transition

state is much less possible.

The reactions of hydrazides and α-ethylhydrazides of organophosphorus acids with phenylisothiocyanate in benzene proceed quantitatively involving the formation of thiosemicarbazides by the scheme:



Kinetics of these reactions is described by the second order rate equation, which can be seen from the linear plot of the reciprocal value of the current concentration vs. time. Rate constants (k) calculated by this equation maintain their constancy both during the process and at various concentrations of the initial reagents and in the presence of reaction products.

Data about substituent effects of various electronic nature in the nucleous on the reactivity of hydrazides of diarylphosphinic, O,O-diarylphosphoric, and O,O-diarylthiophosphoric acids and also of α-ethylhydrazides of O,O-diarylthiophosphoric acids with electrophilic reagents indicate that the reactivity of hydrazine organophosphorus derivatives changes proportionally to the basicity of a nucleophilic reagent [1,2,5,6]. Proceeding from this, one should expect the following order of reactivity of nucleophilic reagents: hydrazide of diphenylphoaphinic acid > α-ethylhydrazide of diphenylphosphinic acid > hydrazide of O,O-diphenylthiophosphoric acid>α-ethylhydrazide of O,O-diphenylthiophosphoric acid > hydrazide of O,O-diphenylphosphoric acid > α-ethylhydrazide of O,O-diphenylphosphoric acid. However, this is not the case with the reactions with phenylisothiocyanate (see the Table). The reactivity of less basic hydrazide of O,O-diphenylphosphoric acid is much higher than that of more basic α-ethylhydrazide of O,O-diphenylthiophosphoric acid.

At the same time one can see from the Table that the

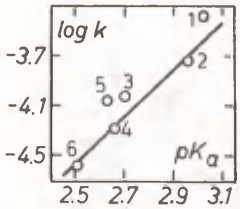
Table

Kinetic Studies of the Reactions of Hydrazides and
α-Ethylhydrazides of Organophosphorus Acids
with Phenylisothiocyanate in Benzene at 25°

NN	Hydrazine derivatives	pK_a	$k \cdot 10^4$, l/mol.sec	α - Effect
1	$(C_6H_5)_2PONHNH_2$	3.02 ± 0.04	4.11 ± 0.23	331
2	$(C_6H_5)_2PON(C_2H_5)NH_2$	2.96 ± 0.04	1.84 ± 0.17	173
3	$(C_6H_5O)_2PSNHNH_2$	2.70 ± 0.04	0.958±0.029	182
4	$(C_6H_5O)_2PSN(C_2H_5)NH_2$	2.66 ± 0.04	0.519±0.018	110
5	$(C_6H_5O)_2PONHNH_2$	2.62 ± 0.04	0.867±0.025	204
6	$(C_6H_5O)_2PON(C_2H_5)NH_2$	2.51 ± 0.04	0.203± 0.012	64

reaction rate constants of α-ethylhydrazides of organophosphorus acids with phenylisothiocyanate change hand by hand with their basicity constants. The plot of lgk vs. basicity constsnts is described by the Brønsted equation (see the Pig.):

$$\lg k = -9.89 + 2.08\ pK_a \qquad (r = 0.994;\ S = 0.073)$$



Plot of lg k vs. pK_a for the reactions of hydrazides and α-ethylhydrazides of organophosphorus acids with phenylisothiocyanate in benzene at 25°.

Numbering of points corresponds to that of compounds in the Table.

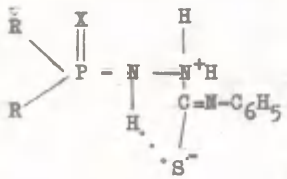
Points characterizing the reactivity of the hydrazides of organophosphorus acids (see the Fig.) do not yield to the common plot of lg k vs. basicity of nucleophilic reagents due to their higher reactivity than it follows from their basicity

Evidently to account for the reactivity of the hydrazides of organophosphorus acids one should take into account not only basicity but also polarizability and the presence of an unshared electron pair on an adjacent nitrogen atom. As we showed elsewhere polarizability effect was insignificant in the reactions studied. Probably the anomalous reactivity of the hydrazine compounds studied results from the effect of the nitrogen atom with an unshared electron pair which is adjacent to the nucleophilic center (the so called α-effect).

To characterize quantitatively the reactivity of hydrazine organophosphorus compounds in the reactions with phenylisothiocyanate we have determined their α-effect. In most cases α-effect is manifested as a positive deviation of the point for α-nucleophile from the Brønsted plot [7]. α-Effect was determined quantitatively as a ratio of the rate constant of hydrazide to the rate constant of arylamine of the same basicity (see the Table). The rate constants of arylamines were calculated by the Brøneted equation which describes the dependence of lgk of the reactions of arylaminee with phenylisothiocyanate on the amine basicities:

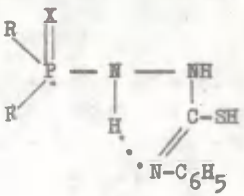
$$\lg k = -9.44 + 1.17\ pK_a \qquad (r = 0.997;\ S = 0.088).$$

One of the causes of increase in the reactivity of the hydrazides of diphenylphosphinic, O,O-diphenylphosphoric, and O,O-diphenylthiophosphoric acids may be in the destabilization of the basic state due to electrostatic repulsion between electrons of adjacent electronegative nitrogen atoms [8]. However, this assumption does not account for the lower activity of α-ethylhydrazides of organophosphorus acids in the reactions with phenylisothiocyanate. Assuming that α-effect is to a large extent determined by the structure of the transition state [3,4], the increase in the reactivity of the hydrazides of organophosphorus acids in the reactions with phenylisothiocyanate is attributable to their ability to form a five-membered cyclic complex, (I) or (II), in the transition state owing to the hydrogen bond between a hydrogen atom of the hydrazide imino group and a sulfur or nitrogen atom of phenylisothiocyanate:



(I)

or



(II)

As one can see from the Table hydrazides of organophosphorus acids manifest the increased reactivity in the reactions with phenylisothiocyanate. However, their activity is characterized by low values of α-effect. At the same time in the reactions with phenylisocyanate the reactivity of phosphorus-containing hydrazides is high enough. α-Effect for the hydrazide of diphenylphosphinic acid is 2772; for the hydrazide of O,O-diphenylphosphoric acid it equals 1783; and that for the hydrazide of O,O-diphenylthiophosphoric acid is 967 [2].

In the reactions of hydrazides of organophosphorus acids with phenylisothiocyanate considerable decrease in the α-effect over that for the reactions with phenylisocyanate can be accounted for by the lower ability of a sulfur atom to form a hydrogen bond. Thus the formation of the cyclic transition state becomes less possible.

Substitution of the ethyl group for a hydrogen atom of the imino group precludes the possibility of the formation of the cyclic transition complex (I) or (II). This leads (see the Table) to the decrease in the rate constants and α-effect for the reactions of α-ethylhydrazides of diphenylphosphinic, O,O-diphenylphosphoric, and O,O-diphenylthiophosphoric acids with phenylisothiocyanate which proceed, evidently, via the step reaction mechanism of the nucleophilic additions of amino containing compounds [9].

Thus the reported results indicate that the α-effect is to a large extent determined by the structure of the transition state. Hydrazine organophosphorus compounds manifest the increased reactivity in the reactions with a certain type of a substrate.

Experimental

Benzene was prepared for kinetic measurements as in Ref. 10. Hydrazides and α-ethylhydrazides of organophosphorus acids were synthesized from the corresponding acid chlorides and hydrazine hydrate or ethylhydrazine by the procedures [11].

Phenylisothiocyanate was purified by distilling in vacuum. Standard solutions of reagents were prepared from freshly purified substances just before kinetic measurements. Before being used benzene was barbotaged with argon to remove dissolved oxygen.

The reaction rate was monitored by the procedure described in Ref. 1.

Basic ionization constants (pK_a) were determined by potentiometric titration via measuring pH of partially neutralized solutions in 50% (w/w) aqueous ethanol at $25\pm0.05^{\circ}$ by the procedure [12].

The accuracy of the results obtained was estimated by the methods of mathematical statistics [13] (reliability is 0.95).

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STUDY OF THE KINETICS OF SOLVOLYSIS OF BIS-CHLOROMETHYLNITRAMINE IN BINARY WATER-ORGANIC SOLVENT SYSTEMS

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The results of the study of the kinetics of solvolysis of I,7-bis-chloro-2,4,6-trinitro-2,4,6-triazaheptane (BCTAH) in binary solvent systems water-DMF and water-acetone are discussed in terms of the solvent effects on the kinetic parameters of the reaction.

The kinetics of solvolysis of I,7-bis-chloro-2,4,6-trinitro-2,4,6-triazaheptane (BCTAH) in binary solvent systems water-dimethylformamide (DMF) and water-acetone has been studied conductometrically:

$$Cl—R—Cl + 2\,H_2O = HO—R—OH + 2\,HCl,$$

$$R: \left[—CH_2N(NO_2)—\right]_3 CH_2—$$

First the absence of the mutual influence of two halogen atoms during their consequent substitution and the first kinetic order of the solvolysis on substrate was established. The results obtained are given in Table I.

It follows from the data of this table that, in accordance with the qualitative Hughes-Ingold theory of the solvent effects[I], the reaction under consideration is accelerated with the increase of the more polar com-

Table I

The Kinetic Parameters of the Solvolysis of BCTAH in Water-Organic Solvents

Solvent	Vol.% org.comp.	Rate constants, $k \cdot 10^4$, s^{-1}					$\Delta H^{\neq}$ kcal/mol.	$\Delta S^{\neq}$ e.u.
		20°C	25°C	30°C	35°C	40°C		
Water-DMF	90.0	0.803	1.43	2.22	(3.67)	(5.89)	17.5 ± 0.5	17.4 ± 1.8
	80.0	(2.49)	3.95	6.03	(9.46)	14.3	15.4 ± 0.3	22.6 ± 0.9
	70.0	5.10	8.08	12.5	20.2	31.0	15.9 ± 0.3	19.3 ± 0.8
	60.0	(9.71)	16.2	24.7	38.6	62.8	16.1 ± 0.6	17.2 ± 1.8
	50.0	18.0	32.2	55.3	(90.2)	(148)	18.4 ± 0.4	8.1 ± 1.6
Water-acetone	90.0	-	0.104	0.143	0.190	0.281	11.5 ± 0.7	42.7 ± 2.2
	70.0	-	0.945	1.63	2.66	4.43	18.4 ± 0.2	15.1 ± 0.6
	60.0	-	2.55	4.11	6.71	12.1	18.5 ± 0.9	12.9 ± 2.9
	50.0	-	7.59	12.6	20.7	32.9	17.6 ± 0.2	13.9 ± 3.0

ponent in the mixed solvent.

In complete agreement with The Electrostatic Theory predictions for the reaction between two polar molecules, in the solvent system water-DMFA one can observe the linear dependence of log k on the reciprocal of the dielectric constant, with the negative slope of the line (Table 2).

Table 2

Parameters of the Linear Relationships $\lg k = \frac{a}{\varepsilon} + b$ for the Solvolysis Rates of BCTAH in Aqueous DMF

t°C	-a	b	r	a	n
20	I90.5 ± 4.3	0.I626 ± 0.0802	0.9995	0.0236	5
25	I8I.4 ± 5.0	0.369I ± 0.0970	0.9989	0.0290	5
30	I65.8 ± 2.4	0.3856 ± 0.0505	0.9998	0.0II2	4
35	I53.4 ± 3.8	0.4755 ± 0.0829	0.9994	0.0I86	4
40	I46.I ± 6.8	0.6583 ± 0.I576	0.9978	0.0356	4

Thus the solvent system effect on the rate constants obeys the Amis equation[2]:

$$\log k = \log k_o - \frac{A}{\varepsilon}$$

where $A = \frac{2\mu_I \mu_2}{kT r^3}$

The absence of linearity between the log k and different functions of the dielectric constant was established for the data obtained in aqueous acetone (Table I); But over the whole temperature range studied and for various compositions of the binary mixture the log k was found to be a linear function of the Grünwald-Winstein ionizing power (Y) (see Table 3).

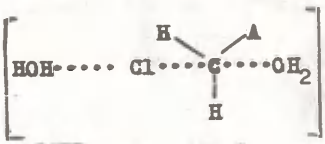
Thus, contrary to the influence of the water-DMF mixtures, which appeared to be connected exclusively with the electrostatic effects, the role of the water-acetone mixtures is complicated by the electrophilic contribution of water molecules participating in the transition state as a polarizing factor for the C—Cl bond[3-5].

Table 3

The Parameters of the Grünwald-Winstein Equation for the Solvolysis of BCTAH in the Water-Acetone Solvents.

t°C	m	-log k_o	r	s	n
25	0.558 ± 0.044	3.995 ± 0.054	0.9937	0.108	4
30	0.583 ± 0.036	3.798 ± 0.044	0.9963	0.087	4
35	0.613 ± 0.029	3.610 ± 0.036	0.9978	0.071	4
40	0.630 ± 0.016	3.400 ± 0.020	0.9993	0.040	4

It is noteworthy that the m-parameter of the reaction series under consideration appeared to be rather small relatively to its value for S_N1-processes[6,7]. Such a result allows us to conclude that water molecules take part in the transition state of the rate-determining step of the reaction as nucleophiles (S_N2 process)[8]:



where A is a remained part of the substrate molecule.

The combined temperature and medium effect for each of the two solvent systems under consideration can be expressed by the following equations:

Aqueous DMF:

$$\lg k = 7.060 - \frac{2015}{T} - \frac{214125}{T \cdot \varepsilon} + \frac{539}{\varepsilon}\ ;\ \Delta \lg k = 0.02.$$

Aqueous acetone:

$$\lg k = 8.360 - \frac{3686}{T} - \frac{460.53}{T} Y + 2.103Y;\ \Delta \lg k = 0.05.$$

The dielectric constants of water-DMF mixed solvents, measured as described elsewhere[9], are summarized in terms of the Åkerlof equation in Table 4.

Table 4

The Åkerlöf Equation ($\lg \mathcal{E} = a - bt$) Parameters for Aqueous DMF at Different Ratios of the Components.

Volume % of DMF	a	$b \cdot 10^3$	r	e	n
50.0	I.8970 ± 0.0028	3.973 ± 0.084	0.999	0.0017	6
60.0	I.85II ± 0.0023	3.630 ± 0.067	I.000	0.00II	6
70.0	1.8246 ± 0.0044	4.019 ± 0.I42	0.998	0.002I	5
80.0	I.7739 ± 0.0032	3.7I0 ± 0.I05	0.999	0.00I6	5
90.0	I.7324 ± 0.0055	3.995 ± 0.I65	0.997	0.0032	6

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KINETICS OF NUCLEOPHILIC ADDITION OF ALIPHATIC AMINES TO ACRYLAMIDE AND ACRYLANILIDE

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The rates of nucleophilic addition of 15 aliphatic amines to acrylamide and acrylanilide in water solution at 25° were determined. The rate constants were correlated by the modified Taft equation with inductive (σ^*) and steric (E_N) parameters.

With the aim to continue the study of nucleophilic addition of aliphatic amines to the activated ethylenic bond [1-3] we have studied kinetics of the reaction:

$$\underset{\text{I}}{R_1R_2NH} + \underset{\text{II}}{CH_2{=}CHCONHR} \longrightarrow \underset{\text{III}}{R_1R_2NCH_2CH_2CONHR} \quad (1)$$

R = H, C_6H_5.

The kinetics was studied spectrophotometrically, uaing the short wave shifts of absorption bands of unsaturated amides II resulting from the addition of amines to their ethylenic bonds.

It should be noted that only a few publications deal with the kinetics of nucleophilic addition to acrylamide (addition of some amino acids [4-6], mereaptopropionic acid [6], morpholine and pyrrolidine [7], methanol and 2-propanol [8], benzenesulfinic acid [10]).

Experimental

Reagents. N-methyl-2-cyanoethylamine was prepared by cyanoethylation of methylamine and purified by twofold distillation through a Vigreux column, b.p. 76°/18mm. Liquid aliphatic amines were purified by the methods described in the literature [11], followed by twofold distillation through a fractionating column of 15 t.p. efficiency. Methyl-, ethyl-, and dimethylamines were purified by twofold recrystallization of hydrochlorides from ethanol. Pure piperidine was prepared by hydrolysis of its N-benzoyl-derivative, recrystallized from hexane-CCl_4 (3:2 by volume). Acrylamide was recrystallized from chloroform, m.p. 84° (lit. 84-85° [12]). Acrylanilide (N-phenylacrylamide) was prepared as described in [13], recrystallized twice from petrol ether, m.p. 103,5° (104-105° [13]). Acrylic acid chloranhydride was prepared according to [14]. β-Pyrrolidinepropionamide and β-morpholinepropionamide were prepared according to [7], recrystallized twofold from methanol, m.p. 75-76° and 95-96°, respectively (lit. 75-76°, 95-96° [7]).

The solutions of acrylamide, acrylanilide and of liquid amines were prepared for kinetic investigations gravimetrically. The solutions of gaseous amines were prepared by decomposition of hydrochlorides with concentrated alkali and absorbtion of amines in water, their concentrations were found titrimetrically with HCl.

Kinetic measurements. Kinetics of reaction (1) in water was followed spectrophotometrically in thermostated cell. 5 to 4000-fold excess of amines was used. 15-20 values of optical density (at 255pm for acrylamide and at 275nm for acrylanilide) were measured up to 30-70% completion of reaction. After the completion of reactions the values of D_∞ were measured. It was assumed that D_∞ and the absorbance of the addition products were identical. The correctness of this assumption

was checked for the products of addition of pyrrolidine and morpholine to acrylamide. Concentration of the product III at the moment of time t_i was calculated from the equation:

$$x_i = \frac{a}{\mathcal{D}_0 - \mathcal{D}_\infty} (\mathcal{D}_0 - \mathcal{D}_i)$$

where a, initial concentration of amide II,
$\mathcal{D}_0$, optical density of reaction mixture at t=0,
$\mathcal{D}_i$, optical density of reaction mixture at $t=t_i$,
$\mathcal{D}_\infty$, optical density of reaction mixture after completion of the reaction.

When the excess of amine was high, pseudo-first-order rate constant was found by the least-squares method and then devided by the concentration of unprotonated amine to give the second order rate constant. If the excess of amine was less than tenfold, the calculations were made according to [2], fitting the data by empirical function.

From 6 to 12 runs for every amine were carried out, using different initial concentrations of the reactants. The rate constant was found as an arithmetical mean of all runs.

Results and discussion

Reactions (1) are practically irreversible and follow first order kinetics for every reactant. They are about 10 times slower than addition of amines to acrylonitrile under the same codditions [2]. Similar ratio of reactivity of acrylonitrile and acrylamide with amino groups of amino acids [4-6] was found by other authors.

Table 1

Rate Constants ($l \cdot mol^{-1} \cdot sec^{-1}$) of the Addition of Aliphatic Amines to Acrylamide and Acrylanilide in Water at 25°

No	Amine	Acrylamide $k \cdot 10^3$	Acrylanilide $k \cdot 10^3$	$\Sigma\sigma^*$	$-E_N$
1	Methylamine	1.9 ± 0.1	2.5 ± 0.1	0.98	0.07
2	Ethylamine	1.19±0.05	1.63 ± 0.08	0.88	0.36
3	n-Butylamine	0.94±0.06	1.26 ± 0.08	0.85	0.40
4	Isobutylamine	0.97±0.08	1.35 ± 0.08	0.86	0.35
5	Cyclohexylamine	0.305±0.007	0.47 ± 0.03	0.83	0.98
6	Allylamine	0.50±0.05	0.66 ± 0.02	1.14	0.20
7	Dimethylamine	71 ± 5	92 ± 4	0.49	0.47
8	Diethylamine	5.2 ± 0.5	8.4 ± 0.4	0.29	1.98
9	Di-n-propylamine	5.0 ± 0.3	7.9 ± 0.4	0.26	2.11
10	Di-n-butylamine	6.4 ± 0.6	11.2 ± 0.7	0.23	2.04
11	Pyrrolidine	64 ± 5	94 ± 9	0.23	0.51
12	Piperidine	34 ± 3	54 ± 5	0.31	0.79
13	Hexamethylene-imine	55 ± 3	89 ± 4	0.29	1.10
14	Morpholine	4.2 ± 0.5	5.8 ± 0.2	1.16	0.79
15	N-Methyl-2-cyano-ethylamine	0.28±0.03	0.34 ± 0.04		

As in previous paper [2] the modified Taft equation (2) was used to correlate rate constants (see Table 2):

$$\lg k = \lg k_0 + \rho^* \Sigma\sigma^* + \delta E_N \qquad (2)$$

Correlation was unsatisfactory, when all available rate constants (except of N-methyl-2-cyanoethylamine for which parameter E_N was unknown) were used. It was improved by the exclusion of the most deviating rate constant (for morpholine). No further improvement was obtained by the exclusion of other relatively more deviating constants (for allylamine, cyclohexylamine, dimethylamine).

Table 2

Results of Correlations

of set	Unsaturated amide	n	lg k_o	$-\rho^*$	σ	R	S
1	Acrylamide	14 [a]	-0.356± ±0.510	2.35± ±0.50	0.581± ±0.258	0.811	0.49
2	Acrylamide	13 [b]	0.367± ±0.314	3.29± ±0.33	0.878± ±0.154	0.951	0.27
3	Acrylamide	12 [c]	0.464± ±0.319	3.47± ±0.36	0.899± ±0.152	0.951	0.27
4	Acrylanilide	14 [a]	-0.199± ±0.504	2.39± ±0.50	0.544± ±0.255	0.822	0.484
5	Acrylanilide	13 [b]	0.522± ±0.305	3.32± ±0.32	0.840± ±0.149	0.955	0.263
6	Acrylanilide	12 [c]	0.618± ±0.309	3.51± ±0.35	0.861± ±0.147	0.955	0.258

n, number of points in the set;

a - N-methyl-2-cyanoethylamine excluded;

b - N-methyl-2-cyanoethylamine and morpholine excluded;

c - N-methyl-2-cyanoethylamine, morpholine and allylamine excluded.

The reactivity of primary and secondary aliphatic amines in reaction (1) fits the same correlation (2) as it was for the previously reported reactions of nucleophilic addition [2].

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KINETICS OF THE REACTION OF PHENYL ACETYLENE WITH ORGANO-MAGNESIUM COMPOUNDS

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Kinetics of the reaction of phenyl acetylene with ethylmagnesium bromide in ethyl ether and with phenylmagnesium bromide in ethyl ether and tetrahydrofurane is studied.

Metallation reactions of acetylenic compounds are being studied intensively. However, reactions involving organo-magnesium compounds have been studied relatively little. To some extent this is due to a restricted number of experimental procedures providing a means for monitoring these reactions.

Kinetics of the reaction was studied by the method of samples. Aliquots were quenched with the deuterium oxide. After mass-spectrometric analysis degree of deuteration of the acetylenic compound was determined. It indicates the degree of metallation of the compound by organo-magnesium compounds reached to the moment of the quench. The detailed procedure is given in the experimental section.

Table 1 lists the second order rate constants. As one can see from Fig. 1 and Table 1 (constancy of the rate constants at various ratios of reagent initial concentrations) the reaction is actually of the second kinetic order.

Table 1

Reaction Rate Constants of Phenyl- and Ethyl-magnesium Bromides with Phenyl Acetylene

Reagent	Initial conc. RMgBr	Initial conc. PhC≡CH	t°C	$k_{II} 10^4 (M^{-1} sec^{-1})$
		Ethyl ether		
	0.87	0,87	38	1.9 ± 0.1
PhMgBr	0.19	0.19	25	0.35 ± 0.01
	0.21	0.20	25	0.40 ± 0.01
	0.16	0.34	25	0.30 ± 0.01
	0.20	0.12	25	0.38 ± 0.04
EtMgBr	0.21	0.21	25	2.92 ± 0.04
	0.21	0.21	25	3.14 ± 0.02
	0.21	0.39	25	2.84 ± 0.05
	0.20	0.10	25	2.87 ± 0.04
	0.20	0.40	25	2.87 ± 0.05
	0.20	0.10	25	2.98 ± 0.05
		Tetrahydrofurane		
	0.24	0.23	15	172 ± 18
	0.23	0.23	15	140 ± 9

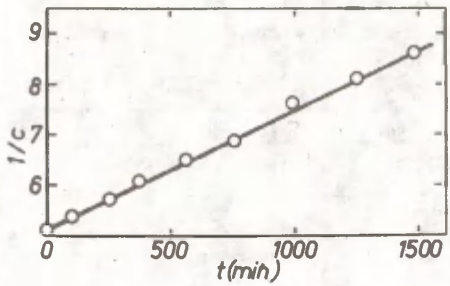

Fig. 1. Graphical determination of the rate constant. Initial concentration of phenylmagneeium bromide is 0.21 M, of phenyl acetylene is 0.20 M; ethyl ether, 25°C.

Table 2

Summary Table of Reaction Rate Constants of Organo-Magnesium Compounds with Phenyl Acetylene

Reagent	Solv.	t°C	$k_{II} \cdot 10^4 (M^{-1} sec^{-1})$
$PhCH_2MgCl$	Et_2O	0	0.008[a]
	Et_2O	37	0.12[a]
	THF	0	84[a]
PhMgBr	Et_2O	25	0.38 ± 0.02[b]
	Et_2O	37	1.2[a]
	Et_2O	38	1.9[b]
	THF	0	10[a]
	THF	15	156 ± 16[b]
EtMgBr	Et_2O	25	3.0 ± 0.2[b]

[a] From Exner and Focker [1]
[b] This work.

Table 2 represents the mean values of the rate constants and also rate constants from Exner and Pocker [1]. The reaction rate constant of phenylmagnesium bromide in ethyl ether (determined by us at 38°) is in satisfactory agreement with that obtained by the above authors with the use of the analogous procedure at 37°C. From our and literature data (Table 2) it follows that reactions of Grignard reagents with phenyl acetylene have relatively high activation energy (about 20-30 kcal/mol) and substitution of tetrahydrofuran for ethyl ether influences significantly the value of the reaction rate constant.

Experimental*

Reagents. Ethyl ether was dried over P_2O_5 and distilled from Grignard reagent in the argon flow.

Tetrahydrofuran was shaken with KOH and distilled over calcium hydride in the argon flow.

Phenyl acetylene was fractionated and distilled in the argon flow.

Argon was passed through the trap filled up with medicine charcoal and multilayer filter from the Petryanov cloth sunk into liquid nitrogen and then through the solution of Na-benzophenone ketyl in the solvent where measurements were carried out.

Organo-magnesium compounds were prepared by the known method from purified halides in the argon atmosphere. The apparatus was heated beforehand at 110°C and cooled in the argon flow. Solutions of organo-magnesium compounds were analyzed acidimetriaally to determine the content of basic magnesium.

Kinetics. Preparation of initial solutions, their transportation, and kinetic experiments were carried out in the

* with participation of M. Haapsal

atmosphere of argon. Flasks were heated beforehand at 110°C and cooled in the argon flow. Preparation of the solutions and kinetic measurements were carried out in the flasks with a side drain to let argon out and take samples. The solutions were transported and the samples were taken with the use of hypodermic syringes.

The reaction flask with the solution of organo-magnesium compound was placed into thermostat. After setting up the temperature a necessary amount of phenyl acetylene was run into the flask. Then a magnetic stirrer was started and the reading of time was begun. At appropriate intervals of time the samples (20 ml) were taken from the reaction mixture and quenched by deuterium oxide. The latter was taken at a rate of 2.5 moles per a mole of organo-magnesium compound. The quenched samples were boiled under reflux condenser for 10-15 min, cooled and centrifugated to remove a residue. The solution was concentrated by fractional distillation of a solvent up to the residual volume 1-1.5 ml. The residue was analyzed on a MKh-1303 mass-spectrometer: nominal energy of ionizing electrons, 14 eV; accelerating voltage, 2 kV; $t° = 20°C$; pressure was 3.10^{-7} atm. From the ratio of peak intensities of molecular ions of deuterated and non-deuterated phenyl acetylenes (peaks m/e 102 and m/e 103) the per cent of deuteration of phenyl acetylene in the sample was determined. The correction for isotopic purity of heavy water was introduced. With regard for initial concentrations of the reagents the concentrations of phenyl acetylene and organo-magnesium compound were calculated at the appropriate moments of the reaction stop.

The reaction rate constants were estimated by the least-squares method from the relationships

$$kt = \frac{1}{c} - \frac{1}{c_o} \quad \text{or} \quad kt = \frac{2.3}{c'_o - c''_o} \lg \frac{c''_o - c'}{c'_o - c''}$$

in the case of equal and unequal initial concentrations of the reagents, respectively.

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Comparative Investigation of Nucleophilic Substitution Reactions at Phosphoryl and Carbonyl Centers. IX.* Non-additive Influence of Alkyl Substituents on Alkaline Hydrolyses of $R_IC(O)OR_2$ and $R_IC(O)SR_2$

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On the basis of recently published data a non-additivity is found in the effects of alkyl groups R_I and R_2 on alkaline hydrolysis rate constants for esters $R_IC(O)OR_2$ and $R_IC(O)SR_2$. Both the nature of these effects in the reaction considered and non-applicability of the isostericity principle to steric effects of substituents OR and SR are discussed.

Strong independence of electronic effects of acyl R_I and leaving R_2 groups on alkaline hydrolysis of carboxylates $R_IC(O)OR_2$ has been demonstrated experimentally several times. (See Refs. 2-4). As a result, the relationship[4]

$$\log k(R_IC(O)OR_2) = a_0 + a_I \log k(R_IC(O)OBt) + \log k(MeC(O)OR_2) \qquad (I)$$

is observed for the esters with wide structural variations, and the estimates[4] of its coefficients a_0 and a_I well coincide with their theoretical values, i.e. with $-\log k(MeC(O)OEt)$ and 1.00, respectively. This relationship breaks only for the esters with α-branched alkyl groups R_I and R_2. The corresponding points significantly deviate to smaller k_2-values from that relationship. The alkyl substituents are now considered as unable to any polar inter-

*For Part YIII see Ref.I.

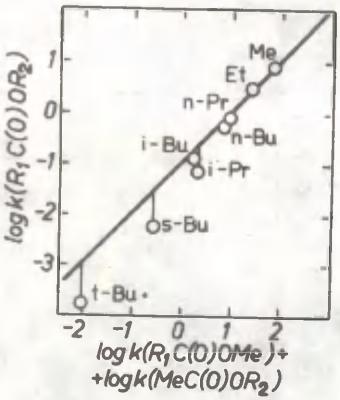


Fig.I. Verification of relationship (I) by the data for alkaline hydrolysis of esters $R_IC(O)OR_2$ with alkyl groups R_I=R_2; 20°, 40% aq. dioxane. The straight line corresponds to the theoretical relationship; see the text.

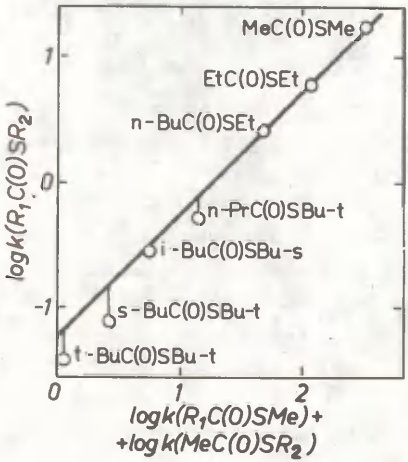


Fig.2. Verification of relationship (I) by the data for alkaline hydrolysis of esters $R_IC(O)SR_2$ with alkyl groups R_I and R_2; 35°, 40% aq. dioxane. The straight line corresponds to the theoretical relationship; see the text.

actions; e.g. see Ref.5. Hence Ref.4 relates the above deviations with some non-additivity in the steric effects of groups R_I and R_2 in this reaction. Such non-additivity should certainly be pronounced for the esters with bulky substituents R_I and R_2.

A good chance to check this assumption can be found in Ref.6. It deals with alkaline hydrolysis, in 40% aq. dioxane, of esters $R_IC(O)OMe$, $MeC(O)OR_2$ and $R_IC(O)OR_2$ with alkyl

Table I

Coefficients and Statistics of Equations[a] (2) and (9) for Alkaline Hydrolysis of Esters $R_IC(O)ZR_2$

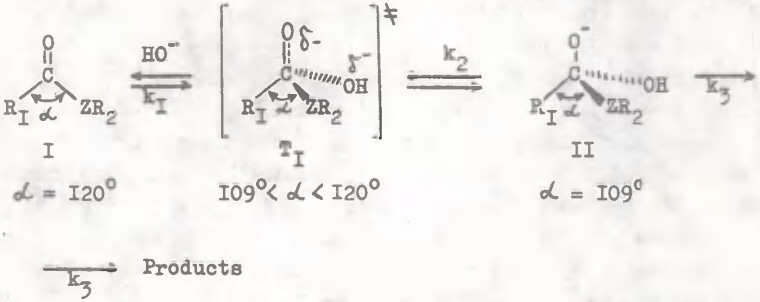
Reg.	Eq.	Z	a_0	a_I	a_2	a_{I2}	n	R	S_0
I-I	(2)	O[b]	0.898± 0.033	I.026± 0.047	I.0II± 0.035	-0.258± 0.039	21[c]	0.998	0.079
I-2	(2)	O[b]	I.0I9± 0.053	I.247± 0.067	I.I92± 0.047	—	22	0.99I	0.I55
I-3	(2)	S[d]	I.250± 0.0I6	I.007± 0.020	I.043± 0.036	-0.I89± 0.038	20	0.999	0.032
I-4	(2)	S[d]	I.286± 0.0I6	I.056± 0.0I7	I.I34± 0.030	—	20	0.998	0.042
I-5	(9)	O[e]	0.878± 0.072	I.00I± 0.III	I.398± 0.I08	-0.478± 0.I28	22	0.989	0.I73
I-6	(9)	S[g]	I.389± 0.085	0.99I± 0.I26	0.2I0± 0.028	-0.050± 0.020	I6	0.990	0.I20

[a]The experimental data are from Refs. 6 and 7. The measures X_I and X_2 are evaluated according to (3) and (4). [b]For 22 carboxylates $R_IC(O)OMe$, $MeC(O)OR_2$ and $R_IC(O)OR_2$ with $R_I = R_2$ = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, s-Bu and t-Bu; see Ref.6. [c]Point for $R_I = R_2$ = Pr-i is excluded because of significant deviation. [d]For 20 esters $R_IC(O)SMe$, $MeC(O)SR_2$ with $R_I = R_2$ = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, s-Bu and t-Bu and $R_IC(O)SR_2$ with R_I, R_2 = Et, Et; n-Bu, Et; n-Pr, t-Bu; i-Bu, s-Bu; s-Bu, t-Bu and t-Bu, t-Bu. [e]For 22 esters, see the footnote ([d]), except those with R_2 = n-Bu, i-Bu and s-Bu.

groups R_I and R_2. The data[7] from the same laboratory for alkaline hydrolysis, in the same solution but at 35°, of esters $R_IC(O)SMe$, $MeC(O)SR_2$ and $R_IC(O)SR_2$ with alkyl groups R_I and R_2 are also considered. Figs. I and 2 show unambiguously that relationship (I) is not applicable to esters with α-branched alkyl groups R_I and R_2 in both series. The points

for such esters deviate, to the lower values of k from the straight lines with slopes I.00 and with intercepts -log k(MeC(0)OMe) or -log k(MeC(0)SMe), respectively. Thus, bulky alkyl groups R_I and R_2 influence non-additively on the free energy changes in alkaline hydrolysis of both O- and S-esters. The smaller non-additivities for the latter esters corroborate steric origin of these influences. Being substantially longer than bond C-O, bond C-S in these esters leads to farther spatial separation of groups R_I and R_2 than it is possible in the corresponding O-esters.

Non-additivity of steric effects of groups R_I and R_2 in the reaction considered is apparently related with an additional destabilization of its transition state T_I. This destabilization is due to an increase in steric interaction, i. e, in mutual repulsion, of groups R_I and ZR_2, Z = O or S, related with decrease in the angle between them in the course of rehybridization of carbonyl carbon from its sp^2 initial state I to sp^3 one in a tetrahedral reaction intermediate II.



A retarding character of this interaction well agrees with an assumption that the reaction rate-controlling step is an addition of OH^- anion, i.e. $k_{obs.}=k_I$; see Refs. 4 and 8. Non-additive influence of alkyl groups R_I and R_2 on the hydrolysis of esters $R_IC(0)ZR_2$, Z = O,S, is well described (see Table I, Regs. I-I and I-3), in agreement with PPL[9,10], by the equation

$$\log k(R_IC(O)ZR_2) = a_0 + a_IX_I + a_2X_2 + a_{I2}X_IX_2 \qquad (2)$$

when one defines scales X_I and X_2 of the effects of R_I and R_2 as follows[9,10] *

$$X_I = \log k(R_IC(O)ZMe) - \log k(MeC(O)ZMe) \qquad (3)$$

$$X_2 = \log k(MeC(O)ZR_2) - \log k(MeC(O)ZMe) \qquad (4)$$

taking groups $R_I = R_2 = Me$ as standard ones. The estimates found for a_0, a_I and a_2 well converge with their theoretical values[9,10] $a_I = a_2 = 1.00$ and $a_0 = \log k(MeC(O)ZMe) = 0.903$ for Z = O (Ref.6) or 1.24 for Z = S (Ref.7). Coefficients a_{I2} are statistically significant for both series and $a_{I2}X_IX_2 \leqslant 0$, since $X_I, X_2 < 0$ for all groups R_I and R_2. Excluding the cross-terms (see Table I, Regs. I-2 and I-4), one immediately finds significantly biased estimates of a_I and a_2 for both Z = O and S as well as a biased estimate of a_0 for Z = O.

An Analysis of Scales X_I and X_2

A very accurate relationship, with a slope being equal to 1.00, between the scales X_I for O- and S-esters (see Table 2, Reg. 2-I) reveals a deep similarity in the effects of those groups in two series. In accordance with Reg. 6, both scales X_I are in good linear dependence upon steric constants(see Regs. 2-2 and 2-3) $E_s(R_I)$**. Such correlation confirms strongly the assumption of purely steric effect of alkyl groups R_I on alkaline hydrolysis of esters considered (cf. Ref.7). For the O-esters, a correlation between the scales X_I and X_2 for the same substituents R is rather poor (see Reg. 2-4). However, since both sets of X_2 measure actually the effect of group ZR_2, a satisfactory linear correlation (Reg.2-5) is observed between the X_2-values for O-esters and steric constants for groups CH_2R_2 that are usually considered[12,14] as isosteric with groups OR_2. A poorer standard deviation for

*Equation (2) transforms to (I) when $a_{I2} = 0$; see Ref.4.
**We use the steric constants E_s revised recently in Ref. II.

Table 2

Coefficients and Statistics for Various Regressions[a]

$y = a_0 + a_I x$

Reg.	y	x	a_0	a_I	n	r	s_0
2-I	X_I^S	X_I^O	-0.048± 0.024	I.073± 0.030	8[b]	0.9977	0.039
2-2	X_I^O	$E_s(R_I)$	-0.078± 0.03I	0.997± 0.042	8[b]	0.9948	0.055
2-3	X_I^S	$E_s(R_I)$	-0.I34± 0.047	I.066± 0.064	8[b]	0.9895	0.085
2-4	X_2^O	X_I^O	0.020± 0.2I5	I.3I9± 0.269	8[b]	0.8943	0.358
2-5	X_2^O	$E_s(CH_2R)$	0.0I8± 0.088	I.393± 0.II2	8[b]	0.98I0	0.I55
2-6	X_2^O	$X_I^O(CH_2R)$	0.I70± 0.036	I.224± 0.060	4[c]	0.9976	0.037
2-7	X_2^S	$E_s(R)$	-0.I83± 0.065	0.44I± 0.088	8[b]	0.8977	0.II7
2-8	X_2^S	$E_s(CH_2R)$	-0.I8I± 0.072	0.4I6± 0.092	8[b]	0.8795	0.I27
2-9	X_2^S	$E_s(CMe_2R)$	+0.253± 0.052	0.205± 0.0I5	4[d]	0.9948	0.044

[a]The measures X_I are from Table 3. Steric constants E_s are from Ref.II. [b]For groups Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, s-Bu and t-Bu. [c]Only for groups Me, Et, i-Pr, and n-Bu. [d]For groups Me, Et, i-Pr, and t-Bu. For other groups R constants E_s are unknown for substituents CMe_2R.

the last regression over that for Reg. 2-2 shows an accuracy available for modelling of steric effect of group OR by that for the substituent CH_2R.

Since the rate-controlling step in the reaction is an addition of anion OH^- to the ester carbonyl group, the susceptibilities of log k - values to steric effects should be equal[4] for both its substituents R_I and R_2O. A similar way is observed, for example, in equlibrium hydration of ketones and aldehydes[I3]. Hence, the fact that in Reg. 2-5 a slope is

larger than I.00 may be explained within the assumption that coefficient a_I in the relationship*

$$E_s(ZR) = a_0 + a_I B_s(CH_2R) \quad (5)$$

for Z = O is also larger than I.00. This assumption is strongly confirmed by non-unity slope found in equation (Reg.2-6)**

$$X_2(R) = a_0 + a_I X_I(CH_2R) \quad (6)$$

Such equation one can derive assuming that groups CH_2R and OR are actually isosteric.

For S-esters the scale X_2 should also have a steric nature, since it measures a difference in the effects of two groups SR and MeS and the abilities of substituent SR to inductive effect*** and to resonance interactions are apparently independent of alkyl moiety R. A low quantity of a correlation (see Reg.2-7) between this scale and constants E_s for corresponding alkyls R is not surprising. However a correlation (Reg.2-8) with constants E_s for groups CH_2R is also poor (Cf. with the results for $X_2(OR)$), i.e. a steric effect of group CH_2R is rather a bad model for steric requirements of substituent SR. In other words, equation (5) appears to be unapplicable to steric effects of substituents SR. On the other hand, there exists an excellent correlation (Reg.2-9) between the X_2-values of four groups SR with R = Me, Et, i-Pr and t-Bu and constants E_s for corresponding alkyls CMe_2R. It shows that S-atom in its steric requirements is more resembling group CMe_2 than group CH_2 as it is assumed by the isostericity principle. The Reg. 2-9 slope is much smaller than I.00. Hence, there

*Equation (5) is a mathematical form of isostericity principle as it is defined in Ref. I2. In this equation a_0 = O and a_I = = I.00 in accordance with the definition.

**Equation (6) is equivalent to the relationship

$$\log k(MeC(O)OR) = A + B \log k(RCH_2C(O)OMe) \quad (6a)$$

Its slope B should be equal to I.00, if the isostericity principle is really applicable to groups CH_2R and OR.

***One can conclude that $\sigma^*(SR)$ = Const for all alkyl groups R, since $\sigma^*(Alk) = 0$.

is no real isostericity between groups SR and CMe_2R, but the LFER principle is only applicable to these steric effects. The smaller value of a_I in Reg.2-9 comparing with that in Reg. 2-5 may be explained by longer bond (=C)-S, i.e. the more spatially removed groups R_2 in the S-eeters have consequently the smaller steric effect than the same groups in the corresponding O-esters. According to Reg. 2-9, the steric constants of groups SR and CMe_2R should be linearly related*

$$E_s(SR) = a_0 + a_I E_s(CMe_2R) \qquad (7)$$

with a slope a_I being much smaller than I.00.

Comparing Regs. 2-5, 2-2 and 2-9 one can see an increase in their slope with decreasing length of the bond (=C)-Z for Z = O, CH_2, and S. The steric effect of OR is more intensive than that of the modelling group CH_2R since bond (=C)-O is shorter than (=C)-C. On the other hand, steric effect of group SR has lower intensity than the corresponding effect of the modelling group CMe_2R, since bond (=C)-S is much longer than (=C)-C. Hence, an increase in the length of the bond (=C)-Z decreases the steric effect of substituent ZR, Z = O, CH_2, and S, because of its progressive removal from the reaction center. This assumption is confirmed strongly by the excellent correlation found between the value of a_I in Regs. 2-5, 2-2 and 2-9 and the length**, l (Å), of the corresponding bond (=C)-Z

$$a_I = (4.899 \pm 0.021) + (-2.580 \pm 0.014)\, l \qquad (8)$$

$$n = 3 \qquad r = 0.9999 \qquad s_0 = 0.004$$

Thus, we want to emphasize once more that steric effects of

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*The present results disagree with the Charton's conclusion[13] that the isostericity principle, i.e. equation (5) with $a_0 = 0$ and $a_I = 1.00$, is well-applicable to steric effects of groups OR and SR.

** These are as large as 1.36, 1.51, and 1.82 Å for bonds[15] (=C)-O, (=C)-C, and (=C)-S, respectively. The last one is assumed to be equal to a C-S -bond length in sulfides; see Ref.15.

substituents ZR with Z = O and S do not apparently equal those of alkyl groups as it is required by the isostericity principle. In spite of that, the LFER principle appears to be well applicable to these steric effects. This principle only assumes that good linear relationships have power between the steric constants E_s for these substituents ZR and the corresponding "isotopological" hydrocarbon groups. It is noteworthy that groups CMe_2R are isotopological for substituents SR while for substituents OR isotopological ones are groups CH_2R.

Since the combined effect of two groups R_I and ZR_2 in alkaline hydrolyses of esters $R_IC(O)ZR_2$ is well described by non-additive equation (2) and the effects of those groups have rather steric origin*, one can assume that their influence should also follow the equation

$$\log k(R_IC(O)ZR_2) = a_0 + a_IE_s(R_I) + a_2E_s(ZR_2) + a_{I2}E_s(R_I)E_s(ZR_2) \quad (9)$$

In this equation, $E_s(R_I)$ is steric constant of R_I; $E_s(ZR_2)$ is steric constant for the corresponding alkyl that is considered as isotopological for group ZR_2, and a_0 + a_{I2} are the model coefficients. The corresponding multiple regressions are collected in Table I (Regs. I-5 and I-6). The regressions have good statistical indices, statistically significant cross-terms and their estimates for a_I and a_2 are in good agreement with the corresponding ones in Table 2. The negative cross-terms in both regressions show a destabilizing role of steric interactions between substituents R_I and ZR_2 in the reaction transition state. The differences observed between standard deviations S_0 of these regressions and those for Regs, I-1 and I-3 are apparently related with the accuracies of Regs. 2-3 and 2-5 in Table 2.

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* Since polar and resonance effects of groups ZR_2 are apparently independent of alkyl group R_2, the terms corresponding to those interactions in the total effect of the substituent ZR_2 should be constant.

Table 3

Measures X_I and X_2 for Effects of Groups R_I and R_2

Substituent	Z = O		Z = S	
	X_I^a	X_2^b	X_I^a	X_2^b
Me	0.000	0.000	0.000	0.000
Et	-0.I38	-0.3I7	-0.I8I	-0.260
Pr-n	-0.427	-0.450	-0.5I5	-0.372
Pr-i	-0.547	-I.030	-0.702	-0.48I
Bu-n	-0.476	-0.524	-0.573	-0.442
Bu-i	-0.982	-0.629	-I.I20	-0.446
Bu-s	-I.I04	-I.320	-I.232	-0.624
Bu-t	-I.473	-2.358	-I.588	-0.840

[a]According to Eq.(2) on the basis of the data in Refs. 6 and 7. [b]According to Eq. (3) on the basis of the data in Refs. 6 and 7.

All regressions of that paper are treated, using computers "Odra-I304" and "Nairi-S" and the multiple regression analysis program based on algorythms of Ref, I6.

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Comparative Investigation of the Nucleophilic Substitution Reactions at Phosphoryl and Carbonyl Centers. X. Effects of Acyl and Leaving Group Structures on Alkaline Hydrolysis of Phenyl Thionphosphinates

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The alkaline hydrolysis rate constants are measured spectrophotometrically for esters of some p-substituted phenols and dimethyl, methylphenyl and diphenyl thionphosphinic acids, $R_1R_2P(S)OAr$, in I:I (v/v) aqueous ethanol at 25°C. A satisfactory applicability of the LFE principle to the effects of acyl and leaving groups as well as a practical additivity of these effects are found in the reaction studied. On the other hand, a substantial non-additivity in the effects of acyl substituents R_1 and R_2 on the rate constants is found.

Alkaline hydrolysis reactions for thionphosphinates are poorer investigated kinetically than similar reactions for phosphinates[I-5]. However, the data measured up-to-date in our laboratory give a chance to estimate, perhaps as a first approximation, the character of co-operative effect of acyl and leaving group structures of esters $R_1R_2P(S)OAr$ on their reactivities in this reaction. Table I collects the second-order rate constants k_2, $l \cdot mole^{-1} sec^{-1}$, for alkaline hydrolysis reaction of $Me_2P(S)OC_6H_4Y$-p (I), $MePhP(S)OC_6H_4Y$-p (II) and $Ph_2P(S)OC_6H_4Y$-p (III) in I:I(v/v) aqueous ethanol at 25°C. These values are measured spectrophotometrically under pseudo-first-order conditions with sodium hydroxide in a large excess. The experimental technique used is similar to that described in Refs. 6 to 8.

Table I

Bimolecular Rate Constants k_2 of Alkaline Hydrolysis of Beters $R_IR_2P(S)OC_6H_4Y$-p

Y	k_2, l mole^{-I}sec^{-I}		
	$Me_2P(S)OAr$	$MePhP(S)OAr$	$Ph_2P(S)OAr$
NO_2	9.866±0.280[5]	5.226±0.093[a]	0.I9I±0.007[b]
Br	0.676±0.0I4[5]	0.589±0.0I0[a]	0.0I29±0.0002[b]
H	0.276±0.006[5]	0.I92±0.008[a]	0.0035±0.0000[b]
Me	0.I72±0.006[5]	0.I07±0.002[a]	0.00I73±0.0000I[b]

[a]It is measured in the present paper. [b]Corrected values. Ref.4 lists the following values of k_2: 0.I42±0.004 (NO_2), 0.0088±0.0003 (Br); 0.00397±0.0008 (H), and 0.00I70±0.00006 (Me).

The data for series I and III have been previously reported in Refs. 4 and 5. Esters II, as well as I and III, are prepared by interaction of methylphenylthionphosphinyl chloride with the corresponding phenols. The former is prepared by a cleavage of MePhP(S)(S)PPhMe, using the method described in Ref.9. All esters II are controlled by TLC (plates "Silufol", Chsechoslovakia), VPC and PMR methods.

The aroxy leaving group effect on rate constants in the series I-III follow accurately the substituent constants σ^o as it has been found in alkaline hydrolysis of m,p-substituted phenyl benzoates[I0], phenyl acetates[7,8], phenyl tosilates (Ref. II) and phenyl diphenylphosphinates[6]. Regs. I, 2, and 3 in Table 2 list parameters and statistics of Hammett-Taft equations for series I to III, respectively. These sets have high sensitivities to the leaving group effects, $a_I = \rho$ (see Table 2). They are much higher than the ρ-values for corresponding carboxylates in 50% aq. ethanol[7,8,I0] but are comparable with a ρ-value for m,p-substituted phenyl phenylsulphonates[II,I2]. One may also see a slight dependence of the values of ρ in Regs. I to 3 on the acyl part substituents in the thionphosphinates.

Table 2

Coefficients and Statistics of Various Linear Regressions $y = a_0 + a_I x$

Reg.	y	x	a_0	a_I	n	r	s_0
I	log k(I)[a]	$\bar{\sigma}^o$	-0.565± 0.028	I.7I8± 0.060	4	0.998	0.048
2	log k(II)[b]	$\bar{\sigma}^o$	-0.7I3± 0.03I	I.624± 0.066	4	0.998	0.052
3	log k(III)[c]	$\bar{\sigma}^o$	-2.46I± 0.032	I.973± 0.069	4	0.998	0.055
4	log k(I-III)[d]	X	0.7I8[1]	I.00[1]			
5	log k(I-III)[e]	X	-0.354± 0.I07	I.053± 0.I27	3	0.993	0.I65
6	log k(I-III)[f]	X	-I.038± 0.058	I.202± 0.069	3	0.998	0.089
7	log k(I-III)[g]	X	-0.809± 0.078	I.I34± 0.093	3	0.997	0.I2I
8	log k(I-III)[d]	pK_a^i	30.567± I.896	-6.475± 0.406	3	0.998	0.08I
9	log k(I-III)[e]	pK_a^i	30.84I± 5.833	-6.767± I.249	3	0.983	0.250
I0	log k(I-III)[g]	pK_a^i	32.859± 4.959	-7.303± I.062	3	0.989	0.2I3
II	log k(I-III)[f]	pK_a^i	34.723± 4.339	-7.757± 0.929	3	0.992	0.I86
I2	log k (I-III)[d]	pK_a^h	I.5I2± 0.3II	-5.85I± I.275	3	0.979	0.26I
I3	log k(I-III)[g]	pK_a^h	I.678± 0.4I5	-8.II2± I.70I	3	0.97I	0.348
I4	log k^S(I-III)[d]	log k^Q(I-III)[k]	-I.674± 0.087	I.534± 0.063	3	0.999	0.053
I5	log k^S(I-III)[e]	log k^Q(I-III)[k]	-2.856± 0.I77	I.623± 0.I28	3	0.996	0.I08
I6	log k^S(I-III)[g]	log k^Q(I-III)[k]	-3.498± 0.098	I.745± 0.07I	3	0.999	0.060
I7	log k^S(I-III)[f]	log k^Q(I-III)[k]	-3.888± 0.039	I.849± 0.028	3	0.999	0.024

[a]For series I. [b]For series II. [c]For series III. Constants $\bar{\sigma}^o$ are from Ref. II. [d]For Y = NO_2. [e]For Y = Br. [f]For Y = Me.

[g]For Y = H. [h]The values of $pK_a(H_2O, 25^\circ)$ for acids $R_IR_2P(O)OH$ Those for R_I, R_2 = Me and R_I, R_2 = Ph are from a collection in Ref. I5. For R_I = Me and R_2 = Ph, the value of pK_a = 4.I9 is estimated according to Ref. I5. [i]The values[I4] of pK_a(50%(v/v) aq.ethanol, 25°C) for acids $R_IR_2P(O)CH_2COOH$. [k]A correlation between log k($R_IR_2P(S)OAr$) and log k for alkaline hydrolysis of corresponding phosphinates[I6] $R_IR_2P(O)OMe$ in methyl cellosolve at 75°C. [I]In accordance with the definition of X; see Eq. (I).

The Acyl Structure Effect. A succesive substitution of Me for Ph-group in acyl part of the thionphosphinate increases its alkaline hydrolysis (see Table I). Similar effect is also observed in alkaline hydrolysis of carboxylates; phenyl acetates MeC(O)OAr are more readily hydrolyzed in alkaline solution than phenyl benzoates PhC(O)OAr; Of. data of Refs. 7 to 9.The LFE principle is also well-applicable to the acyl part structure effect in series I to III. Indeed, there is a good linear relationship between the log k -values of any two sets of esters $R_IR_2P(S)OC_6H_4Y_I$ and $R_IR_2P(S)O\text{-}C_6H_4Y_2$, $Y_I \neq Y_2$, with varying structure of their acyl parts; see Fig. I. Hence, the scale X of the acyl part structure effect on that reaction may be constructed operationally in accordance with PPL[I3], i.e. as the following difference

$$X = \log k(R_IR_2P(S)OC_6H_4NO_2\text{-}p) - \log k(MePhP(S)OC_6H_4NO_2\text{-}p) \qquad (I)$$

According to Table I, X is 0.276, 0.00 and -I.437 for series I, II, and III, respectively. Regs. 4 to 7 in Table 2 show good statistics for the equation

$$\log k(R_IR_2P(S)OAr) = a_0 + a_IX \qquad (2)$$

that describes the acyl effect on the reactions of $R_IR_2P(S)OC_6H_4Y\text{-}p$ when Y = NH_2, Br, H, and Me, respectively. The estimates of the coeffisient a_I in these regressions are found to be practically independent of the substituent in the leaving aroxy group.

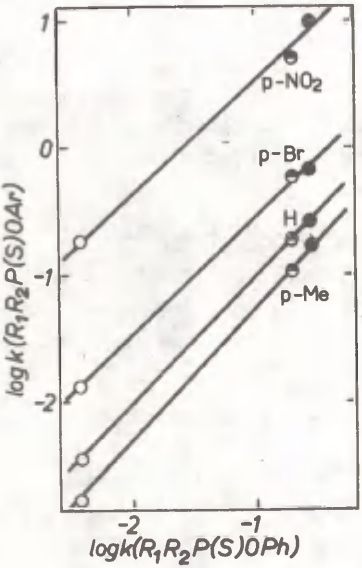

Fig.I. An applicability of the LFE principle to structural effect of acyl group on alkaline hydrolysis of thionphosphinates. Points ◯, ◒ and ● correspond to diphenyl, methylphenyl and dimethyl thionphosphinates.

It is noteworthy that values of log k for alkaline hydrolysis of $R_IR_2P(S)OC_6H_4Y\text{-}p$ with any Y are in good linear relationship, see Regs. 8 to II in Table 2, with pK_a's of acids $R_IR_2P(O)CH_2COOH$ measured[14] under the same conditions. A poorer correlation also exists with pK_a's for acids[15] $R_IR_2P(O)OH$ in water solution at 20-25°C; see Refs. I2 and I3 in Table 2. These correlations appear to claim some deep similarities in the nature of effects of groups R_I and R_2 on the free energy changes in these three processes. On the other hand, between log k -values for alkaline hydrolysis of esters $R_IR_2P(S)OAr$ and methyl esters of corresponding phosphinic acids, $R_IR_2P(O)OMe$, studied by Haake and coworkers[16] in 40% aq. methyl cellosolve at 75 °, there are rather excellent correlations; Regs. I4 to I7 in Table 2. These ones obviously demonstrate the same type of the acyl structure effect in both series. The last relationship is of great importance,

since it shows apparently, together with a similar way of the leaving aroxy group effects in alkaline hydrolyses of phosphinates and thionphosphinates[4-6], an identity of detailed mechanisms of two reactions or their great similarity at any rate.

A Co-operative Effect of Acyl and Leaving Groups. Good applicabilities of the LFE principle to the acyl and leaving group effects on alkaline hydrolysis of thionphosphinates assume that a co-operative effect of those two factors in this reaction should follow accurately the equation

$$\log k(R_1R_2P(S)OAr) = a_0 + a_1X + a_2Y' + a_{12}XY' \qquad (3)$$

Here X and Y' are measures of structural effects of acyl and leaving groups, respectively, in this reaction; and a_0 to a_{12} are coefficients. When one defines, in accordance with PPL, these measures as follows*

$$X = \log k(R_1R_2P(S)OC_6H_4Y_0) - \log k(MePhP(S)OC_6H_4Y_0) \qquad (4)$$

$$Y' = \log k(MePhP(S)OC_6H_4Y) - \log k(MePhP(S)OC_6H_4Y_0) \qquad (5)$$

Y_0 is a group Y accepted as a standard one, the equation (3) coefficients a_0, a_1 and a_2 should obey the following conditions[15] $a_0 = \log k(MePhP(S)OC_6H_4Y_0)$ and $a_1 = a_2 = 1.00$. These restrictions allow to reveal an actual significance[17] of a cross-term $a_{12}XY'$ that describes a non-additivity in the effects related with measures X and Y' in the series considered.

Table 3 lists the results of statistical treatment of the data of Table I within the framework of Eq.(3) for $Y_0 = H$ (Reg. 1), $Y_0 = NO_2$ (Reg. 2) and $Y_0 = \bar{\sigma}^o$ (Reg.3). The equation describes well all rate constants measured in this paper. The estimates for coefficients a_0, a_1 and a_2 in Regs. 1-A and 2-A coincide well with theoretical values, and the estimates for a_{12} are statistically significant but rather small. Excluding non-additive terms from these regressions does not worsen their accuracies (see Regs. 1-B and 2-B) and causes no biasings in the estimates of a_0, a_1 and a_2. The

* Series II is taken arbitrary as a basis for scales X and Y', since the corresponding rate constants are between those for series I and III.

similar situation is also observed in Regs. 3-A and 3-B where constants $\bar{\sigma}^{o}$ are used as the measure of leaving aroxy group effect. Thus, structural effects of acyl and leaving groups in alkaline hydrolysis of thionphosphinates are, at first approxymation, independent. At any rate, their non-additivity, if it actually exists, appears to be small. Similar situation is also observed[18,19] in alkaline hydrolysis of the carboxylates $R_IC(O)OR_2$ when both groups R_I and R_2 are not α-branched alkyls[20] or other bulky substituents . On the other hand, structural effects of groups Y_I and Y_2 in alkaline hydrolysis of aromatic sulfonates $Y_IC_6H_4SO_2OC_6H_4Y_2$ are found to be non-additive[21]. Such features in the co-operative effects of acyl and leaving groups on hydrolysis of the esters of three types of acids are apparently related with some features in detailed mechanisms of these reactions. Hence, one can conclude that the far reaching similarities observed in the effects of acyl and leaving groups and in co-operativeness of these effects in alkaline hydrolyses of carboxylates $R_IC(O)OR_2$ and thionphosphinates $R_IR_2P(S)OR_3$ are a result of a large similarity in the mechanisms of two reactions.

Another argument in favour of practical additivity of the effects of acyl and leaving groups in hydrolysis of the esters considered may be found as follows. Let us assume that $a_{12}=0$ in Eq.(3) and introduce into this equation expressions (4) and (5) for X and Y'. Then Eq. (3) for Y_0 = H transforms to the relationship

$$\log k(R_IR_2P(S)OAr) = -\log k(MePhP(S)OPh) + \\ +\left[\log k(R_IR_2P(S)OPh) + \log k(MePhP(S)OAr)\right] \qquad (6)$$

That is, the value of $\log k(R_IR_2P(S)OAr)$ and the sum $\log k(R_IR_2P(S)OPh) + \log k(PhMeP(S)OAr)$ should be linearly related with slope and intercept being equal to I.00 and $-\log k(MePhP(S)OPh) = +0.7I7$ (see Table I), respectively, if the effects of acyl and leaving groups are independent to a large extent. Fig. 2 shows that the experimental data of Table I fit the theoretical straight line within Eq. (6) coordinates with good accuracy and the corresponding regres-

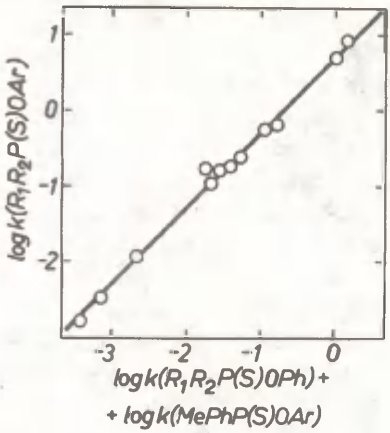

Fig.2. A correlation of log $k(R_IR_2P(S)OAr)$ vs. the sum of log $k(R_IR_2P(S)OPh)$ and log k(MePhP(S)OAr). The straight line corresponds to the theoretical one with slope a_I and intercept a_0 being equal to I.00 and -log k(MePhP(S)OPh) = = + 0.7I7 (see Table I), respectively.

sion is found to be as follows

$$\log k(R_IR_2P(S)OAr) = (0.75I\pm0.032) + (I.0I5\pm0.0I7)\left[\log k(PhMeP(S)OAr) + \log k(R_IR_2P(S)OPh)\right] \quad (6a)$$

$$n = II, \quad r = 0.9988, \quad s_0 = 0.062$$

It does not, however, describe the point (see Fig.2) for $Ph_2P(S)OC_6H_4NO_2$-p .

A Co-operative Effects of Substituents in Acyl Part of Thionphosphinates

We have seen[15,22] that sometimes an effect of groups R_I and R_2 at phosphoryl phosphorus in compounds $R_IR_2P(O)Y$, Y is any reaction center, may be non-additive. A similar situation takes place with the effects of groups R_I and R_2 in alkaline hydrolysis of the esters studied. It is obvious from Fig.3 where the point for MePhP(S)OAr deviates significantly from the theoretical straight line with slope and intercept being equal to I.00 and zero, respectively, in coordinates[22,23] log $k(R_IR_2P(S)OAr)$ and 0.5 $\left[\log k(R_IR_IP(S)OAr) + \log k(R_2R_2P(S)OAr)\right]$ and for Ar = p-$NO_2C_6H_4$*, i.e. the value

*Similar deviations are also observed for all groups Ar studied.

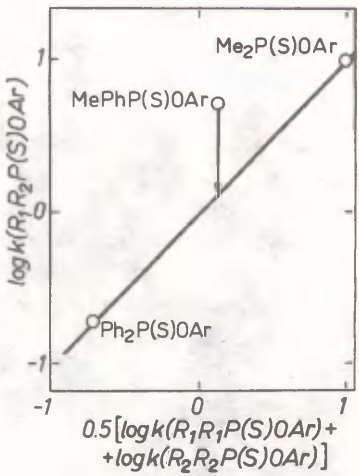

Fig. 3. Non-additivity in the effect of groups R_I and R_2 on alkaline hydrolysis of $R_IR_2P(S)OAr$, i.e. deviation of the point for log k(MePhPS $OC_6H_4NO_2$-p) from the half of sum of the values of log k for esters $Ph_2P(S)OC_6H_4NO_2$-p and $Me_2P(S)OC_6H_4NO_2$-p. The straight line has the theoretical slope, I.00, and intercepts the origin of coordinates.

Table 3

Coefficients and Statistics of Equation (3)

Reg.	a_0	a_I	a_2	a_3	n	R	S_0
I-A[a]	-0.7I4± 0.023	I.009± 0.023	I.034± 0.03I	-0.I02± 0.030	I2	0.999	0.058
I-B[a]	-0.737± 0.033	0.966± 0.029	I.083± 0.038		I2	0.997	0.085
2-A[b]	0.692± 0.054	0.982± 0.054	I.045± 0.044	-0.I33± 0.053	I2	0.997	0.088
2-B[b]	0.737± 0.058	I.097± 0.045	I.088± 0.047		I2	0.996	0.I04
3-A[c]	-0.804± 0.033	I.I43± 0.039	I.702± 0.069	-0.I79± 0.082	I2	0.997	0.085
3-B[c]	-0.82I± 0.038	I.097± 0.039	I.772± 0.074		I2	0.996	0.I0I

[a]The scales X and Y' are based on Equations (4) and (5) for Y_0 = H. [b]The scales X and Y' are based on the same equations, but Y_0 = p-NO_2. [c]The measure X is calculated on the basis of Equation (4) for Y_0 = H whereas constants $\bar{\sigma}^o$ for Y in the leaving aroxy group are used to describe its effect.

of log k for ester PhMeP(S)OAr differs significantly from the half of the sum of log k-values for esters $Ph_2P(S)OAr$ and $Me_2P(S)OAr$ with the same leaving group OAr. This non-additivity is yet seen when one is examining Table I carefully. A substitution of Ph for the first Me-group in series I reduces the reaction rate constant within ca. 20%, whereas a substitution of Ph for the second Me, i.e. II → III, slows down the reaction by a factor of 15 over that for ser.II. We have no special intentions to discuss this non-additivity in the present paper. It is only noteworthy here that this effect may arise as a result of some differences in polar, conjugative and/or steric interactions between two Ph-groups in the initial and transition states for the hydrolysis of diphenyl thionphosphinates, e.g. see Refs. I5, I7 and 22.

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Comparative Investigation of Nucleophilic Substitution Reactions at Phosphoryl and Carbonyl Centers. Part XI. Alkaline Hydrolysis of Phenyl Dimethylthionphosphinates in Aqueous Ethanol. Comparision With Phenyl Acetates

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The alkaline hydrolysis kinetics is investigated for some esters $Me_2P(S)OC_6H_4Y$-p in aqueous solution as well as in 50 and 90 % (v/v) aqueous ethanol at 25°C. The LFER principle is well applicable to the medium effect on this reaction. A combined effect of leaving group structure and solvent mixture composition on the reaction rate constant is found to be substantially non-additive. An experimental reverse in the k dependence upon solvent composition proves the non-additivity strongly. The results obtained for the phosphorus series are compared with those found for phenyl acetates and similarity between the rate-limiting steps in these reactions is assumed.

Effects of the leaving group substituent and the solvent mixture composition on alkaline hydrolysis of phenyl acetates $MeC(O)OC_6H_4Y$-m,p (I) are found to be non-additive[1] to a large extent. Constants ρ for alkaline hydrolysis of esters $Me_2P(S)OC_6H_4Y$-p (II) in water and in 50% (v/v) aq.ethanol also differ substantially[2]. The present paper considers both an applicability of the LFER principle to the ethanol-water mixture composition on the latter process and a co-operative effect of that factor and the leaving group structure in this

reaction. The results obtained are compared with those found in similar investigation[I] for series I. The reaction kinetics for series II with Y = Me, H, Br and NO_2 is measured spectrophotometrically under pseudo-first-order conditions(high excess of sodium hydroxide) at 25°C in water solution as well as in 50 and 90 % (v/v) aq. ethanol. The methods and apparatus used as well as synthesis of the esters have been described previously[2]. Bimolecular rate constants k, I $mole^{-I}sec^{-I}$, (Table I) are obtained by the least-squares method from the pseudo-first-order ones measured in three parallel sets at three to five sodium hydroxide concentrations. For mathematical and statistical treatments the computers "Nairi-C" and "Odra-I304" (Poland) are used.

Results and Discussion

An effect of the aroxy leaving group on alkaline hydrolysis rate constant of esters II follows adequately constants $\bar{\sigma}^{o}$ (Regs. I to 3 in Table 2). Similar effect was also observed in series I. The higher ethanol content in the solvent the higher ρ -value is observed in both series. Constants ρ for series II are higher than the corresponding ones found for series I under the same conditions (Regs.4-6, Table 2).However, there is a good linear relationship (Reg.7) between these ρ values for two series. It shows a higher sensitivity of the constant ρ in series I to solvent composition. A solvent dependent ρ-constant for series II is a result of a strong non-additivity in the structural and medium effects in that series. As a consequence of this non-additivity, the isoparametricity phenomenon[7-9] (IPP) is observed in this reaction,i.e. a reverse of solvent effect on the reaction rate constant with change in the leaving group structure.The rate constants for esters with Y = NO_2, Br and Y = Me, H change in opposite directions with increasing ethanol content in the solvent mixture. Similar behavior was also found in alkaline hydrolysis of esters I in aqueous ethanol.

In series II the solvent composition effect on k also strictly obeyes the LFER principle. The log k - values for the esters with Y = H and NO_2 (Table 2, Regs.8 and 8a;

Table I

Bimolecular Rate Constants k, $l\ mole^{-1}\ sec^{-1}$, for Alkaline Hydrolysis of Esters I at 25°C

Y	%[a]	k	Y	%[a]	k
NO_2	0	5.122±0.072[b]		90	0.819±0.010
	10	6.048±0.162	H	0	0.369±0.006[b]
	30	7.275±0.045		30	0.329±0.006
	40	8.024±0.186		50	0.267±0.006[b]
	50	9.866±0.280[b]		80	0.245±0.003
	70	11.933±0.451		90	0.223±0.006
	80	12.988±0.176	Me	0	0.238±0.004[b]
	90	15.144±0.428		50	0.172±0.006[b]
Br	0	0.629±0.007[b]		90	0.151±0.007
	50	0.677±0.014[b]			

[a] Ethanol content in solvent mixture; in vol.%. [b] From Ref. 2.

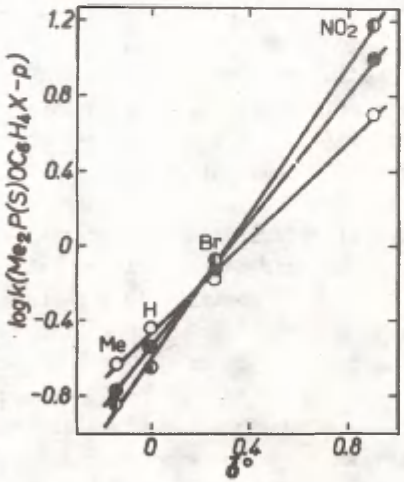

Fig. I. The relationships of log k for alkaline hydrolysis of $Me_2P(S)OAr$ vs $\bar{\sigma}^{\circ}$ in water solution (○), 50% (●) and in 90% (◐) aq. ethanol at 25°C

Table 2

Coefficients and Statistics of Various Regressions

$y = A + Bx$

Reg.	y	x	A	B	n	r	s_0
I	$\log k^{PS},H_2O$	$\bar{\sigma}^{oa}$	-0.464 ± 0.035	1.285 ± 0.075	4	0.997	0.059
2	$\log k^{PS},50\%^b$	$\bar{\sigma}^{o}$	-0.565 ± 0.028	1.719 ± 0.060	4	0.999	0.047
3	$\log k^{PS},90\%^o$	$\bar{\sigma}^{o}$	-0.598 ± 0.031	1.978 ± 0.065	4	0.999	0.051
4	$\log k^{CO},H_2O$	$\bar{\sigma}^{od}$	0.159 ± 0.012	0.946 ± 0.025	4	0.999	0.020
5	$\log k^{CO},50^b$	$\bar{\sigma}^{od}$	0.151 ± 0.020	1.376 ± 0.043	4	0.999	0.034
6	$\log k^{CO},90\%^c$	$\bar{\sigma}^{od}$	0.192 ± 0.029	1.734 ± 0.062	4	0.998	0.049
7	ρ^{PS}	ρ^{CO}	0.466 ± 0.115	0.884 ± 0.083	3	0.996	0.046
8	$\log k^{BS}$ $(Y=NO_2)$	$\log k^{PS}$ $(Y=H)^e$	-0.160 ± 0.079	-2.050 ± 0.142	5	0.993	0.026
8a	"	"	---	-1.773 ± 0.030	5	0.999	0.037
9	$\log k^{PS}$ $(Y=NO_2)$	$\log k^{CO}$ $(Y=NO_2)^g$	0.072 ± 0.061	0.642 ± 0.043	5	0.993	0.024
9a	"	"	---	$0.642 \pm$	5	0.999	0.025
10	$\log k^{PS},H_2O$	$\log k^{CO},H_2O$	-0.679 ± 0.062	1.352 ± 0.114	4	0.993	0.085
11	$\log k^{PS},50\%^b$	$\log k^{CO},50\%$	-0.754 ± 0.035	1.248 ± 0.048	4	0.998	0.052
12	$\log k^{PS},90\%^o$	$\log k^{OO},90\%$	-0.817 ± 0.021	1.140 ± 0.022	4	0.999	0.030
13	A(10+12)	s^{CO},h	-0.679 ± 0.003	-0.187 ± 0.005	3	0.996	0.003
14	B(10+12)	s^{CO},i	1.354 ± 0.005	-0.285 ± 0.010	3	0.999	0.005

[a]Constants $\bar{\sigma}^{o}$ from Ref. 4. For p-Br it is assumed that $\bar{\sigma}^{o} = \sigma^{o}$ (See Ref.5). [b]50% ethanol. [c]90% ethanol. [d]These regressions differ from those in Ref.I because of differences in the scales $\bar{\sigma}^{o}$. The more reliable k value is used here for unsubstituted ester I (See Ref.6) in aqueous solution.

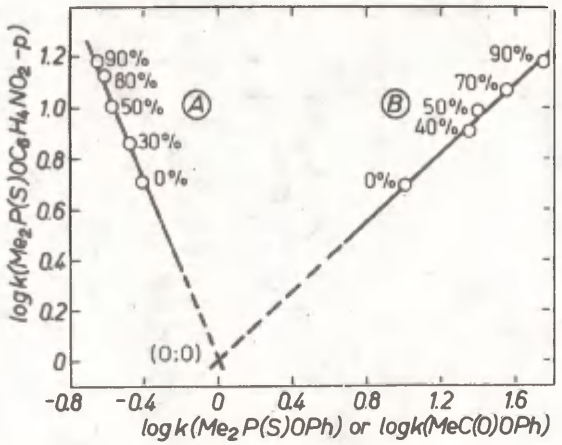

Fig.2. A: Plot of log $k(Me_2P(S)OC_6H_4NO_2-p)$ vs. log $k(Me_2P(S)OPh)$ and B: a dependence of log $k(Me_2P(S)OC_6H_4NO_2-p)$ upon log $k(MeC(O)OC_6H_4NO_2-p)$ in mixtures with varied content of ethanol. The figures correspond to the ethanol content, in vol.%. Both straight lines intersect the point (0;0).

[e]For mixtures with 0, 30, 50, 80, and 90 % of ethanol. [g]The relationship between log k-values for esters I and II with Y = NO_2 in mixtures with 0, 40, 50, 70, and 90 per cents of ethanol. [h]A correlation between the intercepts A in Regs. I0+I2 and S^{co}. [i]A correlation between the slopes B in Hege. I0 to I2 and S^{co}.

Fig. 2,A) are linearly related when ethanol content in the mixture varies from 0 to 90%. This relationship has a negative slope (See Figs. I and 2) and passes through the origin of coordinates.

Since the LFER principle is well applicable to the structural and solvent effects on the hydrolysis of II, the combined

effect of the two factors in this reaction should follow accurately the equation

$$\log k\, a = a_0 + a_I \bar{\sigma}^o + a_2 S^{PS} + a_3 S^{PS} \bar{\sigma}^o \qquad (I)$$

when one defines, in accordance with PPL[9] and with Ref.I, the solvent effect measure operationally

$$S^{PS} = \log k(Me_2P(S)OC_6H_4NO_2\text{-}p,\ i\text{-th mixture}) - \log k(Me_2P(S)OC_6H_4NO_2\text{-}p,\ H_2O) \qquad (2)$$

The corresponding regression that describes adequately the data in water solution as well as in 50 and 90% ethanol is shown in Table 3 (Reg. I). Excluding the cross-term, one finds the worse regression (Reg. Ia in Table 3). Its insignificant term $a_2 S^{PS}$ is in drastic disagreement with Table I as well as with Fig.I. In Reg. I the estimates for a_0 and a_I well coincide with the intercept and slope in the Hammett equation for esters II in aqueous solution (See Reg.I in Table 2). This fact proves that the estimates of Reg. I for coefficients a_0 to a_3 in equation (I) are unbiased. For this series the isoparametric value[7,8] $\hat{\bar{\sigma}}^o = -a_2/a_3$ is as large as 0.I97 that explains the opposite ways of solvent effect on the esters with groups Y = Me, H and Y = Br, NO_2. Table 3 enlists also, for comparision, analogous regressions[I] for hydrolysis of acetates I. They are based on the solvent effect scale S^{CO} constructed similarly to equation (2). There is an excellent linear relationship between the log k - values for esters I and II with Y = NO_2-p measured in the same solvent mixtures when ethanol content varies from 0 to 90%. It passes through the coordinate origin (See Regs. 9 and 9a and Fig. 2, the line R) and reflects homogeneity of solvent effects in two series. That is, there is a deep similarity in mechanisms of solvent effects on the two series. Hence, one can describe the solvent composition effect on series I and II by the same scale, e. g. by the scale S^{CO}. In other words, the rate constants for series II should follow accurately the equation

Table 3

Coefficients and Statistics for Equations (I) and (5)

Coefs. & Stats.	Reg.I k^{PS}	Reg.Ia $k^{PS,a}$	Reg.2 $k^{CO,a,b}$	Reg.2a $k^{CO,a,b}$	Reg.3 $k^{PS,b}$	Reg.4 $k^{PS,c}$
a_0	-0.469±0.026	-0.564±0.070	0.I5I±0.0I9	0.I68±0.0I2	-0.474±0.027	-0.679±0.034
a_I	I.289±0.055	I.660±0.I00	0.952±0.039	0.933±0.036	I.308±0.057	I.357±0.058
a_2	-0.29I±0.082	0.085±0.205	0.043±0.038	---	-0.I82±0.055	-0.I86±0.069
a_3	I.475±0.I74	---	I.062±0.082	I.II2±0.070	0.933±0.II7	-0.29I±0.I00
n	I2	I2	I2	I2	I2	I2
R	0.998	0.984	0.999	0.998	0.998	0.998
S_0	0.046	0.I38	0.034	0.034	0.049	0.052

[a]It differs from that in Ref. I because of differences in the scales of constants $\bar{\sigma}^o$. [b]The solvent effect scale S^{CO} is defined[I] as follows S^{CO} = log k(MeC(O)OØNO$_2$-p, i-th mixture) - log k(MeC(O)OØNO$_2$-p, H_2O). [c]This is a regression $\log k^{PS} = a_0 + a_I \log k^{CO} + a_2 S^{CO} + a_3 \log k^{CO} S^{CO}$. The numerical values of log k^{CO} and S^{CO} are from Ref. I. The more accurate k-value for ester I with Y = H in H_2O is from Ref. 6.

$$\log k^{PS} = a_0 + a_I \bar{\sigma}^o + a_2 S^{CO} + a_3 S^{CO} \bar{\sigma}^o \qquad (3)$$

Here S^{CO} is the solvent effect scale derived[I] from the data for acetates I. Regression 3 in Table 3 corresponds to this equation. This regression and regression I in the table have the same accuracies and their estimates for a_0 and for a_I well coincide.

Since Regs. 2a and 3 for series I and II, respectively, are based on the same scales one can compare them. Thus, series II is more susceptible to the leaving group structure, whereas non-additivity of two effects in this series is lower than that one in series I. That is, in series I varia-

tion of solvent composition exerts stronger influence of the structural effect on the rate constant. That is also seen from the slope found for a linear relationship of $\rho^{o,PS}$ vs $\rho^{o,CO}$ in mixtures considered (Reg.7, Table 2). It should be equal numerically to the ratio of coefficients a_3 in equation (I) for esters II and I. According to Regs. 2a and 3 in Table 3, this ratio is as large as 0.84I. This estimate agrees well with the slope, 0.884±0.083, in Reg. 7 of Table 2.

Measured in the same solvent, the log k-values for esters II and I are related linearly (Regs. I0 to I2, Table 2). Both the intercepts and the slopes of such relationships are linearly related with the scale S^{CO} (Regs. I3 and I4, Table 2). In accordance with the latter regressions, the log k-values measured in the same solvent for esters II and I with the same leaving groups should obey the relationship

$$\log k^{PS} = -0.679 + I.354 \log k^{CO} - 0.I87S^{OO} - \\ - 0.285S^{CO} \log k^{CO} \qquad (4)$$

Here k^{CO} is a rate constant for ester I. Multiple regression analysis of the data for esters II within the framework of the equation

$$\log k^{PS} = a_0 + a_I \log k^{CO} + a_2 S^{OO} + a_3 \log k^{CO} S^{CO} \qquad (5)$$

gives the regression (Reg. 4 in Table 3) whose coefficients well coincide with their counterparts in equation (4). The terms a_2S^{CO} and $a_3S^{CO}\log k^{CO}$ appear to describe different intensities of homogeneous solvent effect on two series as well as different non-additivities of two factors considered on these reactions.

Some Conclusions

Close inspection of the present results shows that alkaline hydrolyses of phenyl esters I and II are similar in some respects:

I. Both reactions are bimolecular, being first-order on substrate and nucleophile concentrations, respectively.

2. The rate constants for two reactions are comparable when

leaving groups, solvent compositions, and temperatures are the same .

3. The leaving group effects in two series are homogeneous.

4. The effect of solvent mixture composition on these two reactions is also homogeneous within the ethanol content variation from 0 to 90 %.

5. Co-operative effect of leaving groups and solvent composition is substantially non-additive in two reactions and the isoparametricity phenomemon is observed in both series.

6. Both processes are isoenthalpic and have comparable activation energies and frequency factors*.

Equation (4) and corresponding regression 4 in Table 3 strongly confirm deep similarity between two reactions and show , in our opinion, that there are no any quantitative differences in the effects of the factors considered on these processes. It is also noteworthy that structural effects of acyl and alcoholic parts on alkaline hydrolyses of esters $R_IC(O)OR_2$ and $R_IR'_IP(S)OR_2$ are practically additive[10]. It seems to be impossible that such similarity is only fortuitous. This similarity requires a close correlation between detailed mechanisms of rate-limiting steps in these reactions. Such step appears to be formation of an intermediate with higher coordination number when anion HO^- attacks molecules of esters I and II.

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* See Part XII. The isoenthalpic way of temperature effect on alkaline hydrolysis of esters I has been found firstly in Ref. II and is shown also by us[1].

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Comparative Investigation of the Nucleophilic Substitution Reactions at Phosphoryl and Carbonyl Centers. XII. Alkaline Hydrolysis of Phenyl Dimethylthionphosphinates in Aqueous Ethanol. The Effect of Temperature and the Reaction Mechanism

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Kinetics of the alkaline hydrolysis of some esters $Me_2P(S)OC_6H_4X\text{-}p$ (I) is measured spectrophotometrically in aqueous solution as well as in 50 and 90% (v/v) aqueous ethanol at 15,35 (partly) and 55°C.With regard for the data measured at 25°C the LFER principle applicabilities to the effects of the leaving group structure, solvent mixture composition,and temperature are shown in the series. A multiple regression is found that describes adequately the influence of these factors on the reaction that is an isoenthalpic process with respect to variation of X. To account for the experimentally observed large similarities in the effects of the above factors on alkaline hydrolyses of esters I and phenyl acetates, the addition-elimination mechanism (7) is proposed for the phosphorus series. It assumes the rectangular pyramidal transition state T_P formation in the rate-limiting addition of anion HO^- to the ester molecule.

In the alkaline solution the esters $Me_2P(S)OC_6H_4X\text{-}p$(I) undergo alkaline hydrolysis[1] as well as various esters of phosphinic[2,3] and carboxylic acids[4,5]. The reaction

Table I

Bimolecular Rate Constants of Alkaline Hydrolysis of Esters I

X	t,°C	k, l mole^{-1} sec^{-1}		
		0[a]	50[a]	90[a]
p-NO_2	15	2.676±0.015	4.013±0.057	
	25	5.122±0.072[1]	9.866±0.280[1]	15.144±0.428[6]
	35			27.377±0.333
	55	35.364±1.033	69.152±2.359	131.609±3.471
p-Br	15	0.329±0.006	0.386±0.007	
	25	0.629±0.007[1]	0.677±0.014[1]	0.819±0.010[6]
	35			2.298±0.081
	55	6.134±0.092	6.272±0.274	8.234±0.127
H	15	0.192±0.002	0.102±0.002	
	25	0.369±0.006[1]	0.267±0.006[1]	0.223±0.006[6]
	35			0.712±0.045
	55	3.029±0.063	2.219±0.062	2.081±0.039
p-Me	15	0.140±0.001	0.061±0.001	
	25	0.238±0.004[1]	0.172±0.006[1]	0.151±0.007[6]
	35			0.309±0.006
	40			0.571±0.015
	55	2.135±0.033	1.542±0.038	1.463±0.022

[a] Ethanol content in the solvent mixture; in volume %.

is bimolecular being first order in the substrate and in anion HO^- concentration respectively. An investigation of the reaction of esters I in ethanol-water mixtures and in water solution at 25°C shows both a good applicability of the LFER principle to the solvent effect in that series and a substantial non-additivity[1,6] in the effects of X and solvent on the reaction rate. In this paper we are studying the alkaline hydrolysis kinetics for some p-substituted esters I in aqueous solution as well as in 50% and 90% (v/v) aq. ethanol at 15, 35 (partly), and 55°C. The bimolecular rate

constants, k, are collected in Table I. where our data for 25°C are also listed. The reaction is investigated spectrophotometrically under pseudo-first-order conditions with sodium hydroxide in a large excess. The experimental and mathematical routine, apparatus used and syntheses of the compounds are described in Refs. I, 3 and 6.

Table 2

The Taft-Hemmett Equation Parameters

EtOH Content,%	t,°C	log k_0	ρ	n	r	s_0
0	I5	-0.706±0.0I7	I.253±0.036	4	0.999	0.028
	25[I]	-0.464±0.035	I.285±0.075	4	0.997	0.059
	55	0.486±0.004	I.I84±0.009	4	0.999	0.007
50	I5	-0.953±0.039	I.767±0.083	4	0.998	0.066
	25[I,6]	-0.565±0.028	I.7I9±0.060	4	0.998	0.048
	55	0.379±0.0I9	I.623±0.042	4	0.999	0.033
90	25[6]	-0.597±0.03I	I.978±0.065	4	0.998	0.052
	35	-0.I89±0.039	I.847±0.083	4	0.998	0.066
	55	0.385±0.035	I.939±0.074	4	0.998	0.059

[a]The constante $\bar{\sigma}^{\circ}$ are from Ref. 7; for p-Br $\bar{\sigma}^{\circ}$ is accepted to be equal to its constant σ° (Ref.9).

In accordance with the results found[I,6] at 25°C, the effect of X on the reaction studied in all solvents as well as at all temperatures follows accurately the equation(Table 1)

$$\log k = \log k_0 + \rho\sigma^{\circ} \qquad (I)$$

Its slope ρ depends on the solvent but not on temperature as it has been observed in the alkaline hydrolysis of phenyl acetates[4] in aqueous solution and in aq. ethanol. The LFER principle is also well applicable[6] to the solvent composition effect on the reaction studied and the k dependence on this factor fits precisely, at any temperature, to the equation[6] (Table 3)

$$\log k_j = \log k_0 + bS \qquad (2)$$

Here b is a susceptibility coefficient, whereas k_j and k_0 are the rate constants in a j-th solvent and in water solution, respectively, and the solvent scale S is derived operationally[6]

$$S_j = \log k(25^\circ C, p\text{-}NO_2, j\text{-th mixture}) - \log k(25^\circ C, p\text{-}HO_2, H_2O)$$

Table 3

Equation (2) Coefficients and Statistics

X	t°C	log k_0	b	n	r	s_0
NO_2	25		I.000[a]			
	55	I.534±0.042	I.I96±0.I32	3	0.993	0.044
Br	25	-0.2I2±0.03I	0.245±0.097	3	0.929	0.033
	55	0.770±0.053	0.252±0.I65	3	0.836	0.055
H	25	-0.435±0.006	-0.467±0.0I8	3	0.999	0.006
	55	0.472±0.028	-0.357±0.088	3	0.97I	0.029
Me	25	-0.628±0.0I5	-0.426±0.042	3	0.993	0.0I6
	55	0.3I8±0.033	-0.358±0.I02	3	0.96I	0.034

[a]In accordance with the definition of the S-scale; see the text.

The slope b depends on X. Equation (2) has poorer statistics for X = Br since $\bar{\sigma}^\circ$ (p-Br) nearly equals the corresponding isoparametric value[6] $\hat{\bar{\sigma}}^\circ$. On the other hand, b does not depend obviously on temperature. The combined effect of X and solvent composition on k in this series follows accurately the equation

$$\log k = a_0 + a_1\bar{\sigma}^\circ + a_2 S + a_3 S\bar{\sigma}^\circ \qquad (3)$$

at I5, 25° (See Ref.6) as well as at 55°C(See Table 4). Excluding the cross-term one finds that its statistics and accuracy worsen substantially. Reality of this term proves strongly the isoparametricity phenomenon[I,6,9] observed at all

Table 4

The Coefficients and Statistics of Equation (3)

Coeffs. & Statistics	Temperature, °C		
	I5	25 (Reg.6)	55
a_0	-0.706±0.030	-0.469±0.026	0.473±0.026
a_I	I.253±0.064	I.289±0.055	I.I80±0.054
a_2	-0.865±0.I49	-0.29I±0.082	-0.229±0.08I
a_3	I.803±0.3I7	I.475±0.I74	I.588±0.I72
n	6[a]	I2	I2
R	0.998	0.998	0.998
S	0.05I	0.046	0.046
$\hat{\sigma}^0$	0.480±0.II8[b]	0.I97±0.060[b]	0.I44±0.053[b]

[a]Based on the data for water solution and for 90% ethanol only.
[b]The standard deviations for σ^0 are estimated in accordance with the error accumulation law[II].

temperatures (See Table I), i.e. a reverse in the rate constant dependence upon a solvent composition with a change in X from Me to NO_2.

Equation (3) coefficients a_I and a_3 are independent of temperature, whereas some increase in a_2 is observed while temperature increases. The estimate for a_2 at I5° is, however, uncertain to a large extent because of lack of the experimental data for 90% ethanol at this temperature*. On the other hand, the isoparametric value $\hat{\sigma}^0$ that is estimated from regression (3) at different temperatures does not depend upon temperature. A similar independence of $\bar{\sigma}^0$ was also found for phenyl acetates[4].

The temperature effect on k follows satisfactorily the Arrhenius equation (Table 5)

$$\log k = \log A + a(I0^3/T) \qquad (4)$$

*Bimolecular constants k are not estimated for these temperature and solvent because of a large scattering observed in the corresponding pseudo-monomolecular constants.

Table 5

Parameters of Equation (4) and Activation Energies, E_a (kcal/mole), for Alkaline Hydrolysis of Esters I.

X	%[a]	log A	a	E_a[b]	n	r	s_0
NO_2	0	9.68±0.21	-0.67±0.06	12.20±0.30	3	0.999	0.020
	50	10.65±0.44	-2.89±0.13	13.21±0.61	3	0.998	0.041
	90	11.56±0.86	-3.10±0.27	14.20±1.23	3	0.996	0.059
Br	0	9.63±1.03	-2.91±0.31	13.30±1.44	3	0.994	0.097
	50	9.69±0.73	-2.92±0.22	13.37±1.02	3	0.997	0.069
	90	11.38±0.60	-3.42±0.18	15.65±0.84	3	0.997	0.057
H	0	9.20±0.38	-2.86±0.11	13.10±0.52	3	0.999	0.035
	50	9.88±0.43	-3.12±0.13	14.31±0.59	3	0.999	0.040
	90	9.69±1.89	-3.06±0.59	14.01±2.69	3	0.982	0.129
Me	0	9.03±0.79	-2.86±0.24	13.08±1.09	3	0.996	0.074
	50	10.16±0.55	-3.27±0.17	14.95±0.77	3	0.998	0.052
	90	10.13±0.72	-3.26±0.23	14.94±1.03	4	0.995	0.049

[a] An ethanol per cent (v/v) in the solvent mixture. [b] $E_a = -4{,}576a$. In accordance with the error accumulation law[11], $s(E_a) = 4.576s(a)$.

in all solvents. In the same solvent, its coefficient a as well as an activation energy $E_a = -4.576a$ do not depend, within their uncertainties, upon X. On the other hand, their clear dependence upon the solvent composition is absent. An Arrhenius equation applicability to any series is equivalent[10] mathematically to the LFER principle applicability to the effect of temperature on this series. Thus, applicability of this principle to the effects of the leaving group structure, the solvent composition, and temperature on alkaline hydrolysis of esters I is the necessary and sufficient condition for an applicability of the polylinear equation

$$\log k = a_0 + a_I\bar{\sigma}^o + a_2 S + a_3\tau + a_4 S\bar{\sigma}^o + a_5\bar{\sigma}^o\tau + a_6 S\tau + a_7 S\bar{\sigma}^o\tau \qquad (5)$$

to the combined effect of these factors on the reaction rate

Table 6

Coefficients and Statistics for Equation (6)

Coefs.& Statistics	"Theor." Values[a]	Calculated Values			
		Reg.I	Reg.2	Reg.3	Reg. 4
a_0	-0.464± 0.035	-0.426± 0.0I9	-0.425± 0.0I8	-0.44I± 0.033	-0.53I± 0.033
a_I	I.285± 0.075	I.265± 0.045	I.256± 0.043	I.257± 0.047	I.6I4± 0.056
a_2	-0.467± 0.0I8	-0.402± 0.079	-0.377± 0.075	-0.269± 0.07I	0.094± 0.II7
a_3	2.86± 0.II	2.864± 0.II2	2.8I2± 0.096	3.009± 0.069	2.898± 0.I36
a_4	I.475± 0.I74	I.509± 0.I64	I.433± 0.I34	I.4I7± 0.I48	--
a_5	--	-0.2I4± 0.237	--	--	--
a_6	--	I.034± 0.408	0.948± 0.344	--	--
a_7	--	-0.268± 0.835	--	--	--
n		36	36	36	36
R		0.997	0.997	0.996	0.987
S_0		0.06I	0.062	0.068	0.I33

[a]See the text.

constant in this series. Here $\tau = (I0^3/298 - I0^3/T)$ is a centered scale[I2,I3]* for temperature. When two ones of the equation variables, $\bar{\sigma}^o$, S or τ, are taken constant, it transforms to the Hammett equation (I), or to equation (2) for solvent effect and to Arrhenius equation. According to Tables 2 and 5 equation (5) will have a non-zero term $a_4 S \bar{\sigma}^o$, i.e. $a_4 \neq 0$, since the equation (I) constant ρ depends on S. This constant as well as coefficient a in equa-

*Ref. I3 shows that such scale decreases substantially a strong non-orthogonality between the columns of $\bar{\sigma}^o$ and S and their products with I/T in the matrix for regression analysis. These non-orthogonalities are a great obstacle for estimation of reliable coefficients of the regression equation.

tion (3) are both independent of temperature. Hence, coefficients a_5 and a_7 in equation (5) should be insignificant. On the other hand, one can't do a reliable conclusion concerning significance of its coefficient a_6. According to the parametrization used, the coefficients a_0 and a_I of that equation should equal the constants log k_0 and ρ in the Hammett equation for esters I in aqueous solution at 25°0; these are -0.464±0.035 and I.285±0.075 respectively; see Table 2. Coefficient a_2 in equation (5) will coincide with b in equation (2) for X = H at 25°C that is as large as -0.467±0.0I8. And the coefficients a_3 and a_4 in equation (5) should be equal to the coefficient a taken with opposite sign in equation (4) for X = H (2.86±0.II; Table 5) and a_3 in equation (3) at 25°C (I.475±0.I74; Table 4), respectively. Table 5 shows applicability of equation (5) as well as some its reduced forms to the experimental data measured. In this Table Reg. I has high quality. Its coefficients a_5 and a_7 are really insignificant while a_6 is found to be non-zero. The estimates for a_0 to a_4 in this regression agree well with their "theoretical" values. Excluding the zero terms has no effect on the regression accuracy and on its other terms (see Reg.2). Further excluding the term $a_6 S\tau$ causes some biasings in the estimates of a_2 and a_3 (see Reg, 3) and a_2 becomes different significantly from its "expected" value. One might consider this biasing as an argument for real significance of this term in equation (5). Both the coefficient a in equation (4) and the activation energy E_a should then be dependent on solvent composition. However, the use of "inner" scales for all factors shows that this term is rather insignificant as it has been found[4] for phenyl acetatee. Hence, Reg. 3 appears to be the true representation of the cooperativeness in the effecte of the factors considered on the alkaline hydrolysis of esters I. And the question of real significance of the term $a_6 S\tau$ in equation (5) remains open for the more thorough studies. Similar situation has been found[4] for alkaline hydrolye-

is of phenyl acetates. The additive model (see Reg. 4) has an unacceptible accuracy. Ite coefficients a_I and a_2 are substantially biased and a_2 is found to be nil.This forces us to state that rate constant k of our reaction does not depend upon solvent. However, such conclusion is in sharp disagreement with the experimental data (see Table I).

Discussion and Some Conclusions

In Part XI of this series[6] we paid some attention to deep similarities in the relationships observed in alkaline hydrolysis of esters I and phenyl acetates. They are as follows.

I. Both processes are bimolecular (first orders on OH^- and an ester concentrations, respectively).

2. The rate constants k for two reactions are comparable when a solvent, a leaving group, and a temperature are the same for both series.

3.The leaving group effects on the rate constants are homogeneous in two processes.

4. The solvent effects on the rate constants in two series are linear within the ethanol content variation from 0 to 90 %.

5. The effects of leaving group structure and solvent composition are substantially non-additive in both reactions.

It is also noteworthy that acyl and alcoholic parts have independent effects on the rate constants in the alkaline hydrolysis of thionphosphinates and carboxylates[14,15].

The present investigation reveals unambiguously that similarity between two series is much deeper, i.e.

I. in these seriee both an activation energy and - constant a in Arrhenius equation do not depend on the ester structure, i.e. both reactions are isoenthalpic processes in respect to the leaving group variation;

2. in both series, the activation energy is practically independent, within its uncertainties, on solvent composition;

3. the mean* values of the activation energies for two ser-

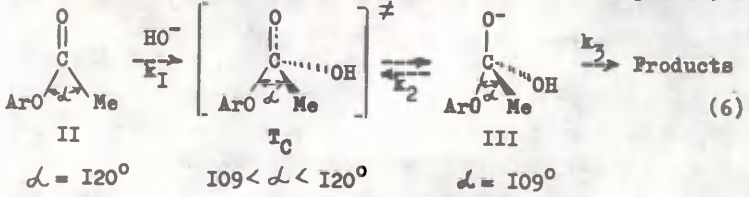
*These values are evaluated from the data for all substituents and solvent mixtures considered. The standard deviations for arythmetic means are also presented[II].

ies are comparable, i.e. I3.94±0.28 and I0.5I±0.22, respectively;

4. the frequency factors in two series are also comparable; log A varies from 9.0 to II.4 in series I and from 7.5 to 9.I for phenyl acetates;

5. the co-operative effects of solvent, leaving group structure and temperature on two reactions are well described by the similar polylinear equations.

To account for these similarities one should assume a large similarity between the rate-limiting steps in two processes. In alkaline hydrolysis of phenyl acetates as well as other carboxylatee with good leaving groups the rate-limiting step is an intermediate III formation[I3-20] (see scheme (6) and Fig. I-A, $k_{obsd} = k_I$ since $k_2 \ll k_3$). Scheme (6) with rate-controlling HO^- attack well rationalised, in our opinion, an



(6)

additivity[I5] in electronic effects of R_I and R_2 on hydrolysis of eeters $R_IC(O)OR_2$ as well as a substantial non-additivity[I8] in steric effects of bulky alkyl groups R_I and R_2 on this process. It also rationalizes the general equation[I7] that describes adequately a co-operative effect of structure, temperature, and solvent on alkaline hydrolysis of ethyl benzoates in various organo-aqueous mixtures. The scheme assumes that solvated anion HO^- attacks the electrophilic reaction center on carbonyl carbon at obtuse angle to the carbonyl group and this attack causes compression in the angle α between the substituents Me and OAr. This compression leads to a substantial increase in steric interactions between these substituents. The transition state T_C structure is intermediate between them for initial ester II and for addition compound III. The additivity in the electronic effecte

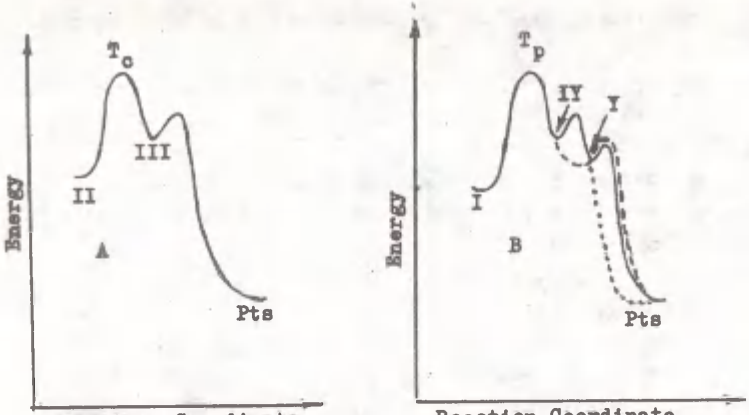


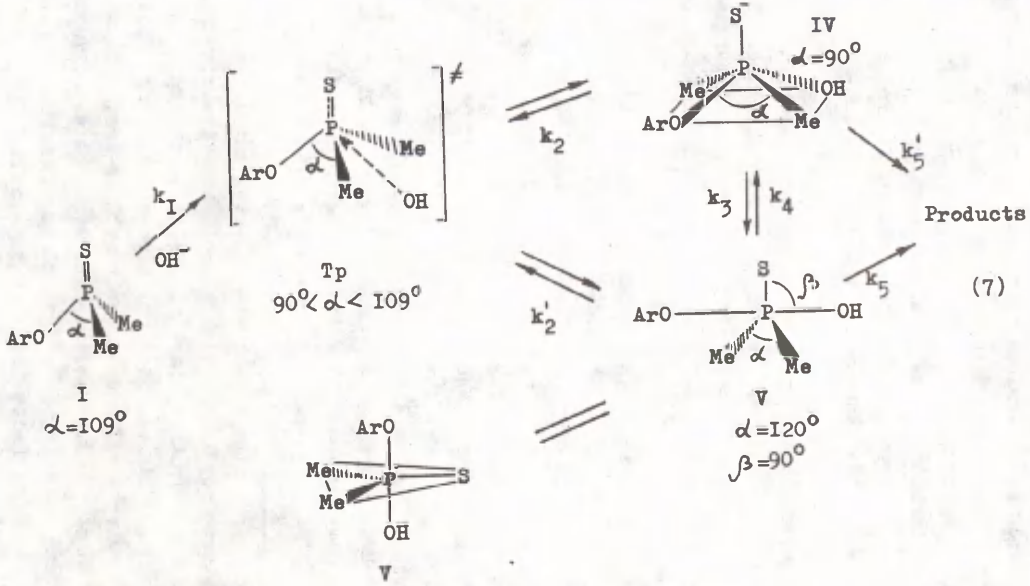
Fig. I. The reaction pathways for alkaline hydrolyses of phenyl acetates (A) and diphenylthionphosphinates (B). Por the latter reaction three possible routes are shown: a) $I \rightarrow T_p \rightleftharpoons IY \rightleftharpoons I \rightarrow$ Products; b) $I \rightarrow T_p \rightleftharpoons IY \rightarrow$ Products and c) $I \rightarrow T_p \rightleftharpoons V \rightarrow$ Products. The heights of barriers correspond to the condition $k_{obsd} = k_I$; k_I is the rate constant for attack of anion HO^- on the ester molecule.

of groups R_I and OR_2 on hydrolysis of $R_IC(O)OR_2$ assumes that the corresponding interactions between the groups do not practically change with formation of new bond in the transition state. Hence, the electronic effects of these groups affect only the effective nucleophilicity of the reaction center.

The mechanism of nucleophilic substitution at tetrahedral phosphorus is a point of large controvercy[21]. Some investigaters assume that it is a one-step reaction[22,23] similar to bimolecular substitution reaction at a saturated C-atom and denote it as S_N2 (P). The others claim that this reaction is a two-step process[2,24] and that a pentacoordinated bipyramidal intermediate. with attacking and leaving groups in apical positions, is formed during the reac-

tion. According to Ref.2 the latter mechanism is the appropriate one for alkaline hydrolysis of phosphinates and thionphosphinates as well, since there is an excellent linear relationship[6] between the rate constants for these two series of compounds. However, it is difficult to account for the similarities found between the alkaline hydrolyses of esters I and phenyl acetates within the above models for the reaction mechaniem for the phosphorus series. To account for these similarities one might assume that anion HO^- reacts with phenyl acetates and with the other carboxylates as well in a bimolecular one-step way similar to the S_N2 reaction. Such hypothesis disagrees however with low activation energies for those reactions as well as with the results of numerous investigations in this field, e.g. see Refs. I9 and 20. Thus, it is more reasonable to assume that alkaline hydrolysis of thionphosphinates is an addition-elimination process with rate --limiting attack of anion HO^-. We assume then that the anion attacks, similarly to the hydrolysis of phenyl acetatee, the phosphorus atom (see Fig. (7)) at obtuse angle to the bond P=S rather than from the opposite* side to this bond. That is, the anion approaches the reaction site between any two of the substituents Me, Me and OAr, e.g. in the plane formed by two bonds P-Me.Similarly to scheme (6),such an attack leads to the compression of the tetrahedral bond angles and leads to formation of a transition state T_p with distorted rectan-

*In such way of the attack the solvated anion would overcome large steric repulsions with three substituents screening the electrophilic reaction center on thicnphosphoryl phosphorus. This way does not also account for both the similar solvent effects on two reactions compared and an increase in steric interactions between the substituents at phosphorus atom in the course of the reaction, i.e. it disagrees with the facts observed experimentally[14].


S⁻
IV
α=90°
Me
OH
ArO
α
Me
k'5
k2
k3
k4
Products
k_I
OH⁻
S
P
Me
ArO
α
Me
I
α=109°
Tp
90°< α < 109°
k'2
S
β
k5
ArO
P
OH
Me
α
Me
V
α=120°
β=90°
ArO
Me
P
S
Me
OH
V

(7)

gular pyramid* structure. Three reaction routes are then possible**. In a three-step pathway (a) the transition state T_P gives first intermediate IY that isomerizes in the energetically more stable form Y with apical groups HO and ArO and the latter form falls further to the reaction products. A second way (b) is a two-step and has the only intermediate IY, whereas in the third pathway (c), being two-step as well, T_P transforms directly in the intermediate Y.

The hypothetical transition state T_P well explains, in our opinion , an additivity in the electronic effects of acyl and alcoholic parts in thionphosphinates on their hydrolysis if one assumes also that formation of the new bond with anion HO^- does not distort the electronic interactions between these substituents. It explains also the homogeneous solvent effects on the reactions compared. The higher activation energies for esters I over those for phenyl acetates may be explained within scheme (7) by more hindered electrophilic center in the former series(Of. (6) and (7)). The proposing mechanism accounts also for a substantial non-additivity[14] in the combined effect of two substituents Ph on hyd-

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* The ground states of stable pentacoordinated phosphorus derivatives ussually have a trigonal bipyramidal[25] structure Y. However, the structure of a rectangular pyramid IY with angle of 104° between the equatorial and axial bonds is found [31] to be only slightly more energetic. But in this paper we are discussing the highly reactive pentacoordinated phosphorus intermediates rather than the stable phosphoranee.

** Formal analysis for the pathway (a) gives $k_{obed} = k_I k_3 k_5/(k_2 k_4 + k_2 k_5 + k_3 k_5)$. It reduces, in accordance with Fig. I-B, to $k_{obsd} = k_I$ when $k_5 \gg k_4$ and $k_3 \gg k_2$ and structure Y is more stable than IY. For pathways (b) and (c) $k_{obsd} = k_I k_5'/(k_2 + k_5')$ and $k_{obsd} = k_I k_5/(k_2' + k_5)$, respectively. These reduce, in accordance with Fig.I-B, to $k_{obsd} = k_I$ when $k_5' \gg k_2$ and $k_5 \gg k_2'$.

rolysis of $Ph_2P(S)OAr$ as well as a similar effect observed in the esters $Ph_2P(O)OMe$*. Steric interactions between the two groups increase in the transition state T_p because of compression of angles α and retard substantially the reaction. In Ref. 2 it has been found that ρ * for an effect of alkyl group on alkaline hydrolysis of $Ph_2P(O)OR$ is unreasonably high, ca. II. Alkyl groups are now considered to be unable to any polar interactions[18,26-29]. It is also well known that constants σ* and E_s for alkyl groups are linearly dependent[30] to a large extent. Thus, the effect found in Ref. 2 seems to have a steric rather than polar origin and it may be related within mechanism (7) with sharp increase in steric interactions between the substituents at P-atom in the course of the formation of the transition state.Hence, mechanism (7) proposed here for alkaline hydrolysis of thionphosphinates is in good agreement with the experimental data collected and well explains the far reaching similarities found between alkaline hydrolyses of these esters and the esters of carbon acids. This scheme appears to be also proper for alkaline hydrolysis of phosphinates.

Computers "Nairi-S" and "Odra-I304" (Poland) are used for treatments of the kinetic measurements and for multiple regression analysis . The regression analysis program is based on the algorymths of Ref. 33 with some our modifications. It reproduced accurately the corresponding tests from Ref.33.

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SOLVENT EFFECTS ON THE ORGANIC COMPLEXES
I. ENTHALPIES OF THE FORMATION OF IODINE COMPLEXES WITH ORGANIC SOLVENTS

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The spectrophotometrically determined enthalpies of the formation of complexes of iodine with organic donors are correlated with donor properties by a linear five-parameter equation of free energies. This relationship may be described accurately enough by a three-parameter equation which takes into account the polarizability, cohesion energy density, and basicity of a solvent : $-\Delta H=1.037 + 4.782\ (n^2-1)/(n^2+2)-15.975\delta^2+0.014\ B$; $R=0.965$. The ΔG values are also correlated by a similar equation. In both cases the most significant parameter is the basicity of solvents.

Solvent effect is of significance for the estimation of organic complex characteristics, especially of equilibrium constants and the formation enthalpies. In the previous papers one can find the data on equilibrium constants determined in such pseudoinert solvents as CCl_4, benzene and even alcohols. It is clear that such results are of only limited value. We know now that CCl_4 forms compounds with many organic donors[1], that the aromatic hydrocarbons interact with both acceptor and donor selective solvents[2], and that cyclohexane and n-alkanes are not indifferent to such a drastic electron acceptor as WF_6[3]. Therefore, when studying the complex formation reactions one must pay more attention to the influence

of solvents which is manifested both in the solvation of all components of the system and in the competitive interaction of solvents with one of the reagents, mainly electron acceptor, which results in decreasing its effective concentration. We have now no satisfactory methods for a simple solution of this problem. Yu.Ya. Fialkov and A.Ya. Borovikov [4-7] showed on the example of dimethylacetamide - iodine complex that the experimental value of equilibrium constant "K" heavily depends on the solvent nature. Even the solvents of such little activity as n-heptane and cyclohexane can solvate some components of the system, both the specific and electrostatic interaction being important.

In the present paper we make an attempt to calculate the influence of organic substances on the characteristics of their complex formation with iodine. Iodine is a classical object of investigations in the sphere of organic complexes (Benesi and Hildebrand [8], Mulliken[9]). The previously published investigations are generalized in the survey of A.N. Terenin[10]. The enthalpies of complex formation with iodine ΔH_{I_2} are the basis for the scale of acid-base parameters, C_A and E_A, of Drago[II]. The attempts to connect the ΔH_{I_2} values with donor properties by a one-parameter equation proved to be unsuccessful. Gutman[I2] reports that the linear dependences exist between ΔH_{I_2} and enthalpies of formation of the complexes with phenol ΔH_{PhOH} and with donor numbers DN, but only the data for six solvents fit to the straight line and data for Pyr and Et_2O deviate significantly. Drago[II] (p.105) showed on a greater number of data that a satisfactory linear dependence between ΔH_{I_2} and ΔH_{PhOH} does not exist despite some trend of proportionality. However Drago's formula: $\Delta H = C_A E_A + C_D E_D$

in which C and E present the covalent and electrostatic characteristics of donor D and acceptor A gives no reliable results. Thus the value of enthalpy for the complex dimethylacetamide - iodine formation calculated by Drago's formula equals only 2.91 kcal/mole, while the experimental value

equals 4.0 kcal/mol in CCl_4 and 3.3 kcal/mol in benzene[II] or 13.6 kJ/mole=3.25 kcal/mole in benzene and 19.8 kJ/mole= =4.72 kcal/mole in cyclohexane [4].

These discrepancies may be partially caused by inaccuracy of the experiment or by difficulties of the procedure treating the results as shown in the works of E.H. Polle[13]. Some difficulties which appear when studying the DMF-I_2 system will be described in the following reports of this series. But the most probable reason for the above mentioned differencies may be the inability of one-parameter equations to take into account the non-specific interactions in the system.

Such a consideration is possible by means of a linear-poly-parameter equation proposed by V.A. Palm and I.A.Koppel for the description of solvent effects on the kinetic, spectral and many other phenomena. Recently we have showed that this equation is applicable for the description of mixing enthalpies [15], extraction[16] and gas absorption processes[17]. Since the spectrophotometrical determination of the values of K and ΔH by means of Benesi-Hildebrand a.o. method always takes place under high excess of donor, it is possible to consider it as a co-solvent.

For the calculations we took the enthalpy data for complex formation with iodine ΔH_{I_2} from Ref.[I] (p.p.190 and 315). But among nearly 150 cited values the data for mathematical treatment are suitable only for 27 solvents for which all the necessary parameters are present in literature. With various values of ΔH the new data obtained by UV-spectroscopy were chosen. Since in Ref.[I] data from many authors are cited, this, on the one hand, may cause the danger of the appearance of definite errors, but on the other hand may give a greater representability.

The ΔH_{I_2}, ΔG_{I_2} data and solvent parameters are given in Table I. The data for solvents N°N° 28-36 are not used in the calculations. As a result we obtained a linear five-parameter equation which correlates the complex formation enthalpies and solvent properties with the correlation

II

Table I

ENTHALPIES ΔH_{I_2} AND FREE ENERGIES ΔG_{I_2} OF COMPLEX FORMATION BETWEEN IODINE AND ORGANIC SOLVENTS AND PARAMETERS OF SOLVENTS

N°	Solvent	$-\Delta H$	$-\Delta G$	$\frac{n^2-1}{n^2+2}$	$\frac{\varepsilon-1}{2\varepsilon+1}$	δ^2	B	E
I	Diethyl ether	4.3	I.3I	0.2I67	0.345	0.057	280	0
2	Tetrahydrofurane	5.3	I.70	0.245I	0.404	0.076	287	0
3	$MeOCH_2CH_2OMe$	3.7	0.I0	0.23I5	0.400	0.09I	238	I.0
4	Dioxane	3.8	-0.05	0.2543	0.223	0.II0	237	4.2
5	Methanol	I.9	0.9I	0.2034	0.478	0.20I	2I8	I4.9
6	Ethanol	4.6	-0.09	0.22I4	0.46I	0.I67	235	II.6
7	tert-Butanol	3.4	I.43	0.234I	0.434	0.I00	247	5.2
8	Ethylacetate	2.5		0.2275	0.374	0.082	I8I	I.6
9	Ammonia	4.8	2.4	0.20I2	0.457	0.2I2	473	I0.6
I0	Triethylamine	I2.0	5.0	0.2430	0.243	0.05I	650	0
II	Diethylamine	9.7	4.2	0.235I	0.3I6	0.06I	637	I.2
I2	Pyridine	7.5	3.03	0.2989	0.44I	0.I04	472	0
I3	Quinoline	7.2	2.82	0.3525	0.423	0.II9	494	0
I4	Acetonitrile	I.9	-0.57	0.2I06	0.480	0.I40	I60	5.2
I5	Dimethylsulfoxide	3.6	I.43	0.372I	0.485	0.225	362	3.2
I6	Dimethylformamide	3.7	0.63	0.2584	0.488	0.I98	29I	2.6
I7	Dimethylacetamide	3.9	I.I4	0.2627	0.48I	0.I99	343	2.4
I8	Benzene	I.45	0.3*	0.2947	0.23I	0.085	48	2.I
I9	Toluene	I.8	0.48*	0.2926	0.238	0.080	58	I.3
20	o-Xylene	2.0	0.6I*	0.2968	0.380	0.08I	68	I.0
2I	p-Xylene	2.I8	0.69*	0.2920	0.229	0.077	68	I.0
22	Mesitylene	2.86		0.2938	0.23I	0.077	77	0.8
23	Fluorobenzene	I.4		0.2768	0.373	0.076	38	0
24	Chlorobenzene	I.I9	-0.24*	0.3064	0.377	0.087	38	0
25	Bromobenzene	I.88		0.3232	0.373	0.096	40	0
26	Iodobenzene	3.2		0.35I8	0.354	0.084	38	0
27	Ethylamine	7.4	3.7	0.2265	0.388	0.086	667	6.0
28	Trimethylen oxide	6.4	I.93	0.2369	-	0.099	282	-
29	Tetrahydropyrane	4.9	I.66	0.253I	-	0.08I	290	
30	Phenetole	0.5	-	0.2979	-	0.I00	I58	-

Table I (continued)

N°	Solvent	$-\Delta H$	$-\Delta G$	$\frac{n^2-1}{n^2+2}$	$\frac{\varepsilon-1}{2\varepsilon+1}$	δ^2	B	E
31	Methylacetate	2.5	-	0.2218	-	0.091	170	-
32	Dimethylaniline	1.83	1.8	0.3225	-	0.095	422	-
33	Sulfolane	2.2	-	0.2849	-	0.133	157	-
34	Tetramethylurea	4.4	-	0.2680	-	0.119	336	-
35	Triethylphosphate	3.2	1.1	0.2455	-	0.068	?	-
36	Tributylphosphate	2.9	1.8	0.2555	-	0.040	283	-

*) Data from Ref.22

coefficient R=0.953. The exclusion of the most deviating data for compound N°27 ($EtNH_2$) from the consideration raises the value of R to 0.968. For remaining 26 points the following equation was obtained:

$$-\Delta H = 0.608 + 7.816\frac{n^2-1}{n^2+2} - 1.006\frac{\varepsilon-1}{2\varepsilon+1} - 18.511\delta^2 + 0.0143\,B - 0.076\,E$$

with R=0.968; s=0.717 and with pair coefficients of correlation r_{01} 0.123; r_{02} 0.048; r_{03} 0.142; r_{04} 0.907 and r_{05} 0.138.

The low values of r_{01} and the corresponding regression coefficients show a small significance of polarity and electrophilicity parameters. This is confirmed by excluding these terms according to Ref.19 which decreases the R values insignificantly. Thus the influence of solvent properties on the ΔH_{I_2} values may be satisfactorily described by the three-parameter equation:

$$-\Delta H = 1.037 + 4.782\frac{n^2-1}{n^2+2} - 13.975\delta^2 + 0.014\,B$$

with R=0.965 and s=0.731. When excluding the next parameters the R value decreases more significantly: for f(δ^2,B) R=0.962; for f(n,B) R=0.912, and for f(n,δ^2) R=0.197 (!). Thus the greatest influence on the ΔH_{I_2} value is exerted by the acid-base interaction between iodine and donor solvents. But the cohesion energy density has a significant influence on the degree of correlation and the less effect is exerted by the solvent polarizability. The negative sign of the regression coefficient at the δ^2 term points to the de-

crease in the ΔH_{I_2} value with the increase in cohesion energy density(with other things being equal).Apparently, for the complex formation it is necessary that the iodine molecule should inculcate into the structure of donor microaggregation held together by the intramolecular forces and overcome the donor molecule association forces (when the equilibrium constants are determined spectrophotometrically, the donor concentration ia dozens and hundreds times higher than the acceptor concentration). Such an interpretation agrees with the concept of lattice structure of liquids according to Ya. I. Frenkel [20] and the hypotheses about the possible microheterogenous structure of solutions[21] .

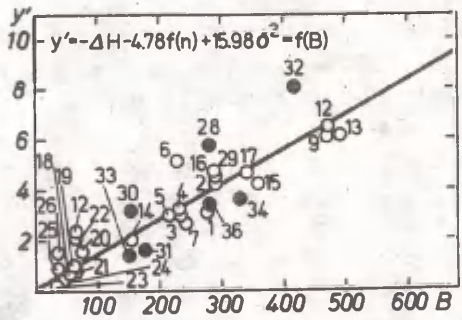

Fig. I. Plot of $y' = -\Delta H - 4.78f(n) + 15.98\delta^2$ vs. basicity B.

The dependence $y' = -\Delta H - 4.78f(n) + 15.98\delta^2 + f(B)$ is illustrated in Fig.I. In the same Figure the crosses correspond to solvents N°N° 28-36 which are not taken into account in the basic calculations and for which the dependence y'=f(B) was calculated by the proposed equations. As one can see the majority of these points approximated satisfactorily the obtained regression line which confirms its reliability. Appreciable deviations exist only for tetrahydropyrane N°28 and dimethylaniline N°32.

The mathematical treatment of data for ΔG_{I_2} (points N°N°I-7, 9-17, 27 in all 17 points,) gives an equation with R=0.954 and after excluding the data for $EtNH_2$ (point N°27) it gives the equation with R=0.968:

$-\Delta G = -2.436 + 1.255\frac{n^2-1}{n^2+2} + 2.777\frac{\varepsilon-1}{2\varepsilon+1} - 8.456\delta^2 + 0.00996B +$

+ 0.046 E with R=0.968; s=0.482 and pair correlation coefficients r_{01}=0.221; r_{02}=0.391; r_{03}=0.405; r_{04}=0.510 and r_{05}=0.386.

The polarizability and electrophilicity terms are of little significance and after their exclusion the three-parameter equation is obtained:

$-\Delta G = -2.040 + 2.360\frac{\varepsilon-1}{2\varepsilon+1} - 5.834\delta^2 + 0.00975\ B$ with R = 0.964 and s=0.463. For the corresponding two-parameter equations the values of R are equal: f(δ^2,B) R=0.961; f(ε,B) R=0.952; f(ε,δ^2)R=0.429.

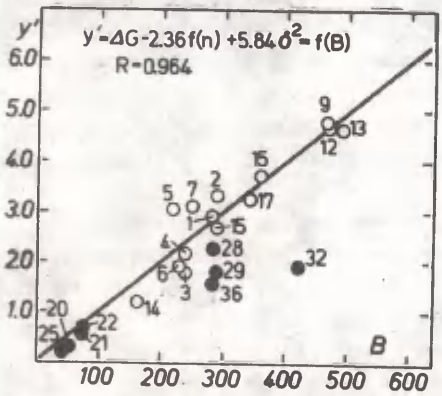

Fig.2. Plot of $y' = -\Delta G - 2.36f(n) + 5.84\delta^2$ vs. basicity B.

Thus analogously to ΔH_{I_2} the factors with the greatest influence on the ΔG_{I_2} value are the basicity of donor, B, and cohesion energy density δ^2. The latter factor hinders the complex formation . It is clear that for quantity $\Delta G = \Delta H - T\Delta S$ free from the contribution of entropy the importance of the δ^2 value is considerably less and of "B" value much higher than in the case of ΔH_{I_2}: the values of corresponding pair correlation coefficients r_{0B} equal 0.405 and 0.951. The dependence $y' = -\Delta G - f(n) + f(\delta^2) = f(B)$ is illustrated in Fig. 2. In order to verify the obtained equation, in Fig. 2 we have denoted with crosses the data for solvents N°N°18-26 and 28-36 which are not

Table 2

ENTHALPIES ΔH_{PhOH} OF COMPLEX FORMATION BETWEEN PHENOL AND ORGANIC SOLVENTS AND PARAMETERS OF SOLVENTS

N°	Solvent	$-\Delta H$	$\frac{n^2-1}{n^2+2}$	$\frac{\varepsilon-1}{2\varepsilon+1}$	δ^2	B	E
I	$POCl_3$	2.5	0.2739	0.464	0.097	146	7
2	Acetonitrile	3.2	0.2106	0.480	0.140	160	5.2
3	Ethylacetate	3.2	0.2218	0.395	0.091	170	?
4	Acetone	3.3	0.2201	0.465	0.095	224	2.1
5	Methylacetate	4.8	0.2275	0.374	0.082	181	1.6
6	Diethyl ether	5.0	0.2167	0.345	0.057	280	0
7	Dimethylformamide	6.1	0.2584	0.488	0.198	291	2.6
8	Dimethylacetamide	6.4	0.2627	0.481	0.199	343	2.4
9	Dimethylsulfoxide	6.5	0.3721	0.485	0.225	362	3.2
10	Pyridine	8.1	0.2989	0.441	0.104	472	0

used in the general calculation. As one can see the results for aromatic solvents satisfactorily approximate the regression line, but for the solvents N°N° 29,32,36 the agreement is worse.

The obtained results give reasonable explanation why the sulfur and selene compounds deflect from the linear dependences between ΔH_{I_2} [11] or ΔG_{I_2} [23] and $\Delta\nu_{PhOH}$ (i.e. basicity of donors). It is for these compounds that values of δ^2 are significantly different from the values for its oxygene analogues and the corrections which they introduce are also higher.

As in Ref.11 the author reports that a linear dependence between the values of ΔH_{I_2} and ΔH_{PhOH} does not exist, we have examined the possibility to use a linear multi-parameter equation in this case. The values of ΔH_{PhOH} were taken from Ref. 12. (Table 2) and the following equation was obtained:

$$-\Delta H_{PhOH} = 5.791 - 4.579\frac{n^2-1}{n^2+2} - 13.830\frac{\varepsilon-1}{2\varepsilon+1} + 13.078\delta^2 + 0.0171\,B + 0.0878\,E$$

with R=0.970; s=0.674 and

pair correlation coefficients r_{01}=0.583; r_{02}=0.119; r_{03}= =0.450 r_{04}=0.943 and=r_{05}0.558.

As the parameters of polarizability and electrophilicity are of negligible significance the equation may be reduced to the form:

$-\Delta H = 4.554 - 11.386\frac{\delta-1}{2\delta+1} + 11.338\delta^2 + 0.0149\ B$ with R= =0.968 and s=0.568.

Thus both ΔH_{I_2} and ΔH_{PhOH} values correlate satisfactorily with donor properties. The greatest influence on them is exerted by the basicity and a little smaller one is exerted by the cohesion energy density. But the values of regression coefficients at separate parameters are different. As a result it is impossible to obtain a satisfactory one--parameter linear relationship $\Delta H_{PhOH}=f(\Delta H_{I_2})$.

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SOLVENT EFFECTS ON THE ORGANIC COMPLEXES II. THE UV-SPECTROPHOTOMETRICAL INVESTIGATION OF INTERACTION BETWEEN DIMETHYLFORMAMIDE AND IODINE

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In the presence of dimethylformamide the decrease and change in UV-absorption bands of iodine dissolved in cyclohexane takes place. With the increase in DMF concentration the absorption band in a visible spectrum (520 nm) shifts towards the shorter wavelengths and the UV band (225 nm) to the longer waves. In the solution of DMF two relatively weak bands at 295 and 370 nm are observed. The complex formation constant, determined by the Benesi-Hildebrand equation, has various values depending on the wavelength at which the measurements were made. The spectrophotometrically determined equilibrium constant depends on the concentration of iodine. There exists a linear relationship between lgK and lgC values.

Though there are many papers [1,2] dealing with the formation of complexes between organic substances and iodine a number of questions are not clear: in particular, solvent effects [3,4]. In the present investigation we give some results of studying the UV-spectra of DMF-iodine system. In Ref. 4 the long wave iodine absorption band at $22.4 \times 10^5 cm^{-1}$ ($\lambda \simeq 445$nm) was determined. The dimethylacetamide-iodine system is studied in detail by Yu.Ya. Fialkov[3] and the dimethylbenzamide-iodine system is considered in Refs. 5,6.

EXPERIMENTAL

UV absorption spectra were studied on a SF-4A spectrophotometer at 20±1°. The cells were from quarz of 1 cm thickness or dismountable with variable thickness. DMF and cyclohexane (grade "Chromatographically pure") were dried and rectified. After sublimation iodine was stored in the desiccator with sulfuric acid. The solutions are obtained by diluting 0.1 m solutions prepared gravimetrically.

RESULTS AND DISCUSSION

The UV absorption spectra of 0.0005 m I_2 solution in cyclohexane (the reference cell contained cyclohexane), 0.001m of I_2 in DMF (the reference cell was filled with DMF) and 0.0001m of DMF in cyclohexane are shown in Fig.1. Iodine in cyclohexane is characterized by two absorption bands - one band is intensive, relatively narrow and assymetric with the maximum at 230-235 nm (Ref.[2] gives the maximum in the range of 145-240 nm) and another is a weaker and wider band in the visible spectrum with the maximum at 520 nm which agrees with Ref.[7]. In the same UV region (220-230 nm) there exists a narrow intensive DMF absorption band character-

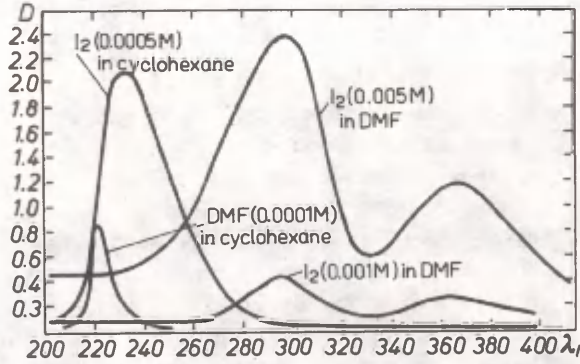

Fig. 1. UV spectra of 0.0005 m I_2 in cyclohexane, 0.001 m and 0.005 m I_2 in DMF and 0.0001 m DMF in cyclohexane.

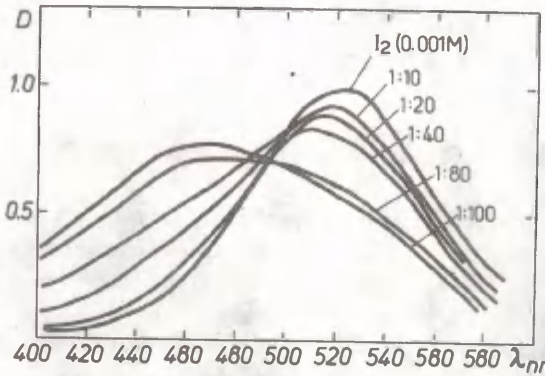

Fig. 2. The shift of I_2 absorption band in cyclohexane λ=520 nm caused by the addition of various amounts of DMF.

istic also of other amides (n-π^* transition).

The I_2 absorption band 235 nm in DMF (the reference cell contains DMF) is considerably weaker, wider and shifted to the greater wavelengths. For the 0.001 m I_2 solution in DMF the optical density at 295 nm is ca four times weaker than for 0.005 m I_2 solution in cyclohexane. The visible band of I_2 absorption is also decreased but the shift occurs to the shorter wavelengths - maximum of absorbance is observed at 370 nm. To make it clearer Fig. 2 illustrates also the absorption spectrum of 0.005 m I_2 solution in DMF. A similar shift and decrease in UV absorption band in the acceptor solutions of $CHCI_3$, CCI_4, and C_2HCI_5 were established for DMF[8].

The literature gives much smaller values for band shifts in the I_2-amide systems, but they were obtained for the I_2 solutions in an inert solvent (usually n-hexane or cyclohexane) in the presence of some excess of amide, but not in the pure amide solution. Thus for the tetramethylurea-I_2 complex Ref. 1 gives (p.209) the charge transfer bands λ=268 or λ=282.

Fig. 2 illustrates a gradual shift of I_2 absorption band in the visible region (520 nm, 0.001 m solution in cyclohexane) with the increase in DMF amounts from 0.01 to 0.1mol/l, i.e. with excess from 10 to 100 with respect to I_2.

Unlike the dimethylacetamide complex[3] in the present case it is impossible to separate absorption bands of bound and free I_2.

The complex formation equilibrium constant "K" was calculated using wavelengths 400-460 nm where the absorption is caused mainly by the complex formation and the free I_2 absorption is insignificant and besides decreased as a result of the partial complexation of iodine. It is found that the optical density value "D" obeys satisfactorily the Benesi-Hildebrand equation: $\frac{a.1}{D} = \frac{I}{\varepsilon_{AB} \cdot K} \cdot \frac{I}{b} + \frac{I}{\varepsilon_{AB}}$

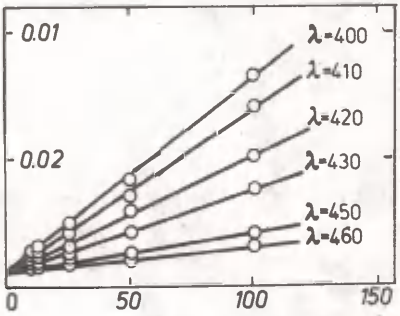

Fig.3. The applicability of the Benesi-Hildebrand equation to the I_2-DMF systeme at various wavelengths.

i.e. a linearity of $\frac{C_{I_2} \cdot l}{D}$ vs. $\frac{I}{C_{DMF}}$ is observed. (Fig.3). However, the calculated "K" value decreases directly with wavelength ca by an order of magnitude with the extinction coefficient being constant (Table 1).

The calculations made with the Scott equation give analoguous results. Such an inconstancy of the determined value "K" depending on wavelength on which the determination was carried out was mentioned in many papers and its possible reasons are considered in Ref. [9]. It should be noted that the obtained values of "K" 7.2±50 are of the same order as those in Ref. [3] for the dimethylacetamide-iodine system K=19.8 (in heptane or cyclohene).

For the system $PhCONMe_2$-I_2 which has weaker donor properties K equals 3.86 ± 0.1[10] only.

Such a dependence of the spectrophotometrically determined

Table 1

THE COMPLEX FORMATION CONSTANTS K AND EXTINCTION COEFFICIENTS ε IN THE SYSTEM DMF-IODINE CALCULATED BY THE BENESI-HILDEBRAND EQUATION FOR VARIOUS WAVELENGTHS

λ	K l/mole	ε
400	7.2	714
410	8	1000
420	11.3	1000
430	15.6	1000
450	35.7	1000
460	50	1000

Table 2

THE COMPLEX FORMATION CONSTANTS IN THE DMF-IODINE SYSTEM AT VARIOUS I_2 CONCENTRATIONS

C_{I_2} mole/l	lgC	K l/mol	lgK
0.01	-2.0	250	2.40
0.005	-2.7	750	2.87
0.001	-3,0	3750	3.57
0.0005	-3.7	5100	3.71
0.0001	-4.0	6125	3.79

values of "K" and, accordingly, ΔG and ΔH values on the wavelength on which the measurements were performed may be one of the reasons responsible for the worse correlation between ΔG (or ΔH) values and the solvent parameters and the discrepancies in the ΔH values which are reported for the same systems by many authors (see Ref.[1]). However, it is

possible that there is another explanation for this phenomenon. In a series of papers the "K" values determined in diluted solutions are informed to depend on the concentration of solutions as a result of changes in the activities[10] or the formation of microaggregates in the solution [11]. Such a phenomenon was established by us for the DMF, pyridine, and benzene - halogenoalkanes systems [12,13].

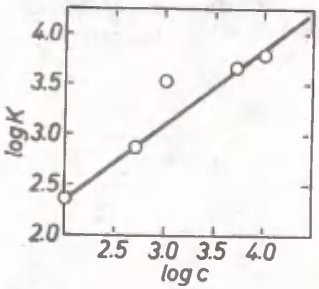

Fig.4. Plot of lgK vs. lgC for the DMF-I_2 system.

In the system DMF-I_2 with the decrease in iodine concentration the value of "K" increases significantly (Table 2). The cited "K" values are calculated on the basis of integral density absorption changes in the visible spectrum at the I_2:DMF ratio I:I by the procedures from Ref.[8]

The plot of lgK vs. lgC is nearly linear (Fig.4) which was established also in the case of the systems with halogenohydrocarbons [8,12,13].

Thus when the "K" (or ΔG) values are determined spectrophotometrically the discrepancies depending on the determination conditions are possible. This influences the results of the methematical treatment and estimation of these data. The errors are less, if using ΔH values or $\Delta\nu$ values, as will be shown in Commun.III.

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SOLVENT EFFECTS ON THE ORGANIC COMPLEXES
III. INFLUENCE OF SOLVENTS ON THE I_2-ABSORPTION BAND SHIFTS.

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The values of the I_2 short and long wave absorption bands are satisfactorily correlated with the solvent properties by the linear free energy five-parameter relationship.

In communication I we have shown that the enthalpies and free energies of I_2 complex formations with organic solvents satisfactorily correlate with the solvent properties by the two-parameter linear equation which take into account the basicity and cohesion energy density of solvents. However, the ΔH and, especially, K_{eq} values which are determined by the UV-spectrophotometric data may differ significantly for the same objects depending on the wave-length on which the measurements are done, the method of calculation, solvent, and even on the concentration [1,2,3]; see also Communication II. Therefore, it is more reasonable to consider the direct experimental data, viz. the changes in I_2 absorption bands in the donor solvents. Therefore, we have verified the possibility to describe the changes in both I_2 long (520 nm) and short wave (235 nm) absorption bands in solvents by the linear five-parameter equation which takes into account various solvent parameters.

In Ref. 4 the authors assume that the main influence on the spectral wave shifts is exerted by the universal interaction, i.e. the nonspecific solvation determined by polar-

ity and polarizability of solvents. However, they recognize that a specific solvation may lead to considerable deviations from the proposed linear relationship

$$hc \times \Delta\nu = C_I f(\varepsilon, n) + (C_2 + C_3) f(n)$$

In Ref.5 where the shift value of I_2 visible absorption band is determined for nearly 50 solvents, it was shown that there exists a linear relationship between $\Delta\nu$ and ionization potential but only for separate groups of solvents of related chemical nature.

The connection between the long wave (visible) I_2 absorption band and the solvent properties was investigated in detail recently in Ref.6 which has shown that for n-donors there exists some correlations with the ionization potential, the function of universal interactions, and, in the case of substituted pyridines, (the so-called Kosowers complexes) with pK. For the π-donors these correlations do not work. However, $\Delta\nu$ of I_2 both for n- and π-donors correlate satisfactorily (R=0.97) with the solvent basicity parameter "B" which is determined as a change in the OD band of MeOD.However, such a correlation of n, π-solvents with $\Delta\nu$ of short wave (UV) of I_2 absorption band does not exist. The authors[6,7] come to the conclusion that in the systems iodine-donor solvents there exist both an "external" complex with the charge transfer D. I_2 (C-T complex I) and an "internal" complex $[DI]^+I^-$ (C-T complex II). The former complex is responsible for the short wave UV-band and the latter for the long wave visible band.

In Commun. I we have shown that the thermodynamic parameters of I_2 complexes with donors may be satisfactorily described by the linear free energy multi-parameter equation. Therefore it was very interesting to verify the applicability of this equation to the correlation of shifts both in long- and short wave absorption bands with solvents parameters. For calculations the data from Ref.[5,6] for the visible band and from the monograph of E.I. Guryanova and coworkers [8]

Table I

SOLVENT SHIFTS OF THE I_2 VISIBLE ABSORPTION BAND

N°	Solvent	λ	$\nu \cdot 10^{-3} m^{-1}$	$\Delta\nu$
I	n-Hexane	523	I9I2	0
2	CCl_4	5I7	I934	22
3	Chloroforme	5I2	I953	4I
4	CH_2Cl_2	506	I976	64
5	Dichloroethane	497	20I2	I00
6	Ethyl chloride	494	2024	II2
7	tert-Butyl chloride	495	2020	I08
8	Ethyl iodide	478	2092	I80
9	Benzene	502	I992	80
I0	Chlorobenzene	508	I969	57
II	Bromobenzene	503	I988	76
I2	Toluene	496	20I6	I04
I3	Iodobenzene	493	2028	II6
I4	Mesitylene	489	2045	I33
I5	Anisole	490	204I	I29
I6	Methanol	440	2273	36I
I7	Ethanol	443	2257	345
I8	n-Propanol	445	2247	335
I9	i-Propanol	446	2242	330
20	Dimethoxyglycole	458	2I83	27I
2I	Diethyl ether	466	2I46	234
22	Di-n-propyl ether	470	2I28	2I6
23	Diisopropyl ether	472	2I29	207
24	Dioxane	452	22I2	300
25	Tetrahydrofurane	446	2242	330
26	Ammonia	430	2326	4I4
27	Pyridine	422	2370	458
28	Diethylamine	4I0	2439	527
29	Triethylamine	4I4	24I5	503
30	Dimethylacetamide	440	2273	35I
3I	Fluorobenzene	507	I973	6I
32	Ethylacetate		2I90	278

Table I (continued)

33	Acetone		2200	288
34	Water		2220	308
35	n-Butanole	448	2230	318
36	Dimethylformamide		2240	328
37	Piperidine		2420	508

Table 2

SOLVENT SHIFTS (RELATIVE TO n-HEPTANE) OF THE I_2 UV-ABSORPTION BAND

N°	Solvent	λ	$\nu \cdot 10^3 m^{-1}$	$\Delta\nu$
I	Methanol	231	4329	127.3
2	Ethanol	233	4292	90.2
3	n-Propanol	236	4237	35.6
4	i-Propanol	236	4237	35.
5	n-Butanol	237	4219	17
6	tert-Butanol	233	4292	90
7	Diethyl ether	250	4000	-202
8	Diisopropyl ether	255	3922	-280
9	Tetrahydrofurane	249	4016	-186
10	Dioxane	264	3788	-414
11	Acetone	242	4132	-69
12	Cyclohexanone	253	3953	-249
13	Ammonia	229	4367	165
14	Ethylamine	246	4065	-137
15	Diethylamine	260	3846	-356
16	Triethylamine	278	3597	-605
17	Piperidine	260	3846	-356
18	Pyridine	235	4255	53
19	Quinoline	238	4202	0
20	Dimethylsulfoxide	276	3623	-579
21	Benzene	292	3425	-777
22	p-Xylene	303	3300	-901
23	Mesitylene	330	3030	-1172
24	Toluene[9]	302	3311	-890
25	o-Xylene[9]	316	3165	-1037

Table 2 (continued)

N°	Solvent	$10^3 m^{-1}$		
26	m-Xylene[9]	318	3145	-1057
27	Cyclohexane[10]	302	3311	-890
28	Acetone[10]	255	3922	-280
29	Water[10]	190	5263	1061

(p.p.204-210) for the UV-band were used. The corresponding λ and ν values are given in Tables 1 and 2. However for the calculations not the values of the spectral frequencies but the shifts of the absorption frequencies $\Delta\nu$ with respect to the absorption frequency in "neutral" solvent, viz. n-hexane, were taken: the long wave λ =523 nm $\equiv \nu$ $1912.10^3 m^{-1}$ and short λ=238 $\equiv \nu$ $4202.10^3 m^{-1}$. It is necessary to emphasize that unlike the data for a visible band the short wave spectrum was obtained, as a rule, for the iodine solutions in a solvent - n-heptane, cyclohexane, or CCI_4 and only in the presence of certain amounts of donors which affects the values of $\Delta\nu$ (vide Commun.II). The properties of solvents are given in our previous communications.

The calculation for all 37 points of the visible frequency shifts gives an equation with R=0.969. The exclusion of the data for the point with maximum deviation N°32 (ethylacetate) raises the R value only negligibly to R= =0.974. We obtain the following equation:

$$\Delta\nu \cdot 10^3 = -74.56 + 221.4\,(n^2-I)/(n^2+2) + 223.6\,(\delta-I)/(2\delta+I) - 114.3\delta^2 + 0.725B + 8.608E \text{ with } R=0.974;\ s=37.24$$

and pair correlation coefficients r_{0I}=0.407; r_{02}=0.364; r_{03}=0.250; r_{04}=0.926, and r_{05}=0.329.

In this way we have confirmed the results of Ref.6 for a greater number of solvents that the main effect on the shift value of I_2 visible band is exerted by the basicity of solvents. The found corresponding pair coefficient is smaller (r_{04}=0.926) than the one from Ref.6 (R=0.970).

This may be explained by the fact that a greater number of solvents including the alcohols capable of self-association participated in the calculations. The estimation of the significance of separate parameters indicates that polarizability and cohesion energy density terms are of small significance contrary to the case of ΔH and ΔG which almost does not influence the value. The latter may be described by the three-parameter equation satisfactorily and by the two--parameter equation somewhat worse:

$\Delta\nu \cdot 10^3 = -16.12 + 210.6\frac{\varepsilon-1}{2\varepsilon+1} + 0.714B + 6.28E$; R=0.972; s=37.0

$\Delta\nu \cdot 10^3 = -54.27 + 0.726B = 8.12E$; R=0.966; s=40.6

$\Delta\nu \cdot 10^3 = -51.68 + 0.711B = 397.7\frac{\varepsilon-1}{2\varepsilon+1}$; R=0.954; s=47.3

In Fig. I the dependence $y' = \Delta\nu - f(\varepsilon) - f(E) = f(B)$ is illustrated.

The signs of all terms of the regression equation are positive. The presence of both nucleophilic and electrophilic solvation of iodine complexes confirms the assumption expressed in Ref.6 about the partially ionized structure of C-T complex II. The growth of polarity of solvents will favor a separation of charges in the complex.

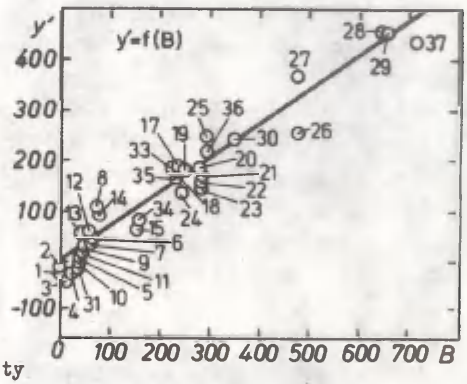

Fig. 1. Plot $y' = \Delta\nu - f(\varepsilon) - f(E)$ vs. basicity of solvents B for I_2 visible frequency shift.

Since Ref. 6 shows that the UV-spectrum charges for iodine complexes (C-T complex I) do not correlate with the basicity "B" of solvents by means of only one equation common for the n and π donor, it was interesting to verify the applicability for this case of a poly--parameter equation. With calculations for 29 substances all (Table 2) the correlation coefficient is low, R=0.918 only.

The successive exclusion of the most deviated points raises the R value: N°19 (quinoline) R=0.941; N°18 (pyridine) R=0.959; N°25 (o-xylene) R=0.966. Thus, the application of a five-parameter equation enables, contrary to the proposed in Ref.6 one-parameter relationship $\Delta\tilde{\nu}=f(B)$, to reach a satisfactory correlation between solvent properties and a value of I_2 UV-band shifts. Relatively low correlation coefficient R=0.966 should be caused by the fact that the $\Delta\tilde{\nu}$ values are determined by many authors in various solvents and at various ratio donor: iodine (see Commun.II).

For 26 solvents the following equation is obtained:

$$\Delta\tilde{\nu}\cdot 10^3 = 91.23 - 5360(n^2-I)/(n^2+2) + 1812(\varepsilon-I)/(2\varepsilon+I) + 1663\delta^2 + 0.213B + 4.20E;\ R=0.966;\ s=138.4;\ r_{01}=0.711;\ r_{02}=0.800;\ r_{03}=0.681;\ r_{04}=0.216;\ r_{05}=0.784.$$

If the relatively unimportant parameters of specific solvation are excluded, we obtain the following three-parameter equation:

$$\Delta\tilde{\nu}\cdot 10^3 = 20.2 - 5709(n^2-1)/(n^2+2) + 1943(\varepsilon-I)/(2\varepsilon+I) + 1716\delta^2;\ R=0.963;\ s=138.1.$$

In contrast to C-T complex II a shift of a spectral band for I_2 C-T complex I is determined only by non-specific solvation factors which agrees with the opinion of the authors of Ref.6 about the non-ionic character of C-T complex I. The exclusion of nonspecific solvation factors leads to the breaking of the correlation: $f(\varepsilon,\delta^2)$ R=0.866; $f(n,\delta^2)$ R=0.899; $f(n,\varepsilon)$ R=0.904. The dependence $y'=\Delta\tilde{\nu}-f(\varepsilon)-f(\delta^2)=f(n)$ is illustrated in Fig. 2.

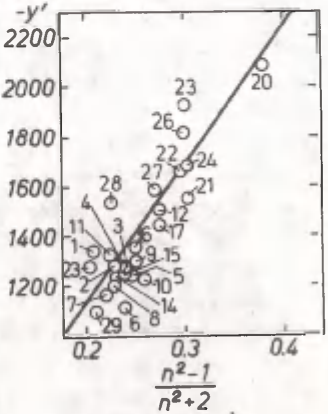

Fig.2. Plot of $y'=\Delta\tilde{\nu}-f(\varepsilon)-f(\delta^2)$ vs. $f(n)$ for I_2 UV frequency shifts.

Over a long period of time there has been disagreement about the applicability of Badger-Bauer principle [11] to the complexes with hydrogen bond, i.e. about the existence of a reliable linear dependence between $\Delta\nu$ and ΔH of the complex formation. In many papers [12] the existence of such a linear dependence is doubted, but Drago and coworkers [13,14] show that this failure is caused by the inaccuracy of the spectrophotometrically estimated values of ΔH. They have shown that for the calorimetrically estimated values of ΔH there exists a satisfactory linear plot vs. $\Delta\nu$.

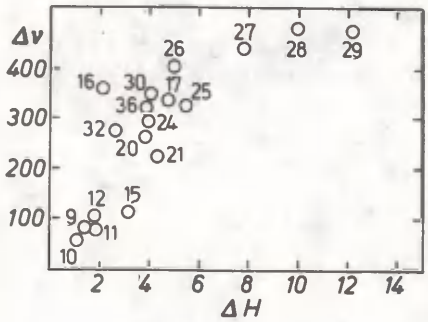

Fig.3. The relationship between ΔH_{I_2} and $\Delta\nu$ for iodine complexes.

The Badger-Bauer principle was established for the phenol complexes. We have verified the existence of the same relationship between ΔH_{I_2} and $\Delta\nu$ for iodine complexes, using the values from Commun. I and III. However, with spectrally determined ΔH_{I_2} values no linear relationship with $\Delta\nu$ was established (Fig.3), though ΔH_{I_2} and $\Delta\nu$ values change hand by hand both in UV and visible ranges. At present the question is open whether the absence of linearity is due to inaccuracy of spectrally determined values of ΔH_{I_2} or for the systems with iodine such a proportionality does exist at all.

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STUDY OF REACTIVITY OF SUBSTITUTED BICYCLO[2.2.2] OCTANES. 1.Formulation of the Problem. On the Methods of Synthesis of Disubstituted Derivatives of Bicyclo[2.2.2]octane

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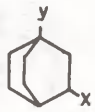
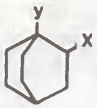
General methods of synthesis of 1,2-, 1,3-, and 1,4-disubstituted derivatives of bicyclo [2.2.2] octane to obtain series of compounds for the systematic study of substituent effects are discussed.

Problem of the attenuation of the so called inductive substituent effect via cyclic systems is still urgent, since the quantitative evidence available cannot be described quite adequately within the framework of a single and non-conflicting theoretical model (see Ref.1). When studying this problem, one can successfully use substituted 1-derivatives of bicyclooctane of the following type as convenient model compounds:

1-y-4-X-



1-y-3-X-



1-y-2-X-

where Y denotes a reaction center and X is a varied substituent.

Series of 1-Y-4-X- derivatives and their analogs were often and successfully used to study the regularities of the attenuation of the inductive effect (Refs. 2-4 and others). Just recently Friedl, Hapala, and Exner have published some data (pK_a in 50 $^{v}/v$ ethanol and 80 w/w methyl cellosolve) for the I-Y-3-X series [29]. The same work gives the pK_a values in the two solvents for the I-Y-2-CN derivative. The authors of Ref. 29 discuss the data obtained and also the data of Roberts and Morelend[2] within the framework of some varieties of the electrostatic model.

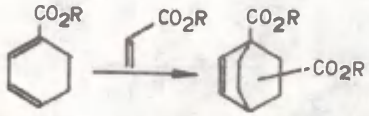
Unfortunately, Ref. 29 presents the conditions of synthesis and purification of the compounds very briefly. It might be as well to have more data characterizing the degree of purify of the isomers obtained. Purity of the preparations is of considerable importance in this case from the viewpoint of estimating the degree of reliability of measuring pK_a or rate constants, since the question is in comparing relatively small values of substituent effects. This is especially important when the data obtained in different laboratories are compared. Thus the pK_a value in 50 $^{v}/v$ ethanol for non-substituted bicyclo[2.2.2] octane-I-carboxylic acid is 6.74 in Ref.2, whereas Ref. 29 gives the value equalled to 6.83. It should be also noted that there is just a rough linear relationship between the pK_a values for 3-substituted series of bicyclo [2.2.2] octane-I-carboxylic acid in 50 $^{v}/v$ ethanol and 80 $^{w}/w$ methyl cellosolve ($r=0.9562$). But the accuracy of these data is of primary importance for estimating the nature of substituent effects for the system studied with enough reliability.

Proceeding from the above, it is of interest to synthesize, purify, and characterize the three series of compounds in the same laboratory. Then the corresponding substituent effects should be characterized quantitatively with respect to various processes, depending on temperature and medium. Uniform and thoroughly verified experimental procedures should be used.

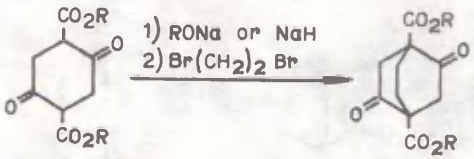
When formulating this problem, another independent one appears, that is the synthesis of the three series of derivatives. It is of interest to obtain the compounds where Y=CO_2H, CO_2R and others, and X = H; halogen, OH(OR), CO_2^-, $NH_2(NR_2)$, NO_2, and $N(CH_3)_3^+$.

From the literature the following general methods of synthesis of derivatives of bicyclo [2.2.2] octane are known:

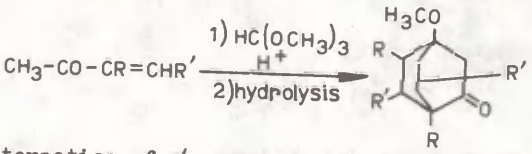
A. Diels-Alder reaction by the scheme[5,6] and others.



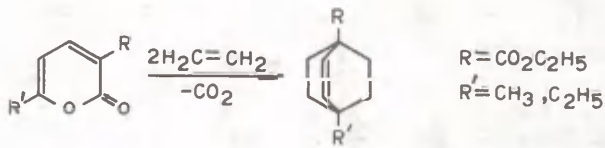
B. Synthesis via derivatives of cyclic di- β -ketoesters [7,8] and others.



C. Acid - catalytic intramolecular cyclization of methylvinylketone with further hydrolysis of an intermediate [9,10] and others.

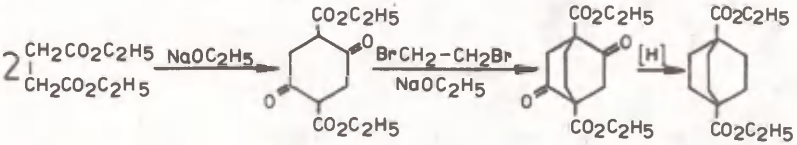


D. Interaction of α -pyrans with two molecules of dienophile (120-165°, 1000 atm.)[11] and others.

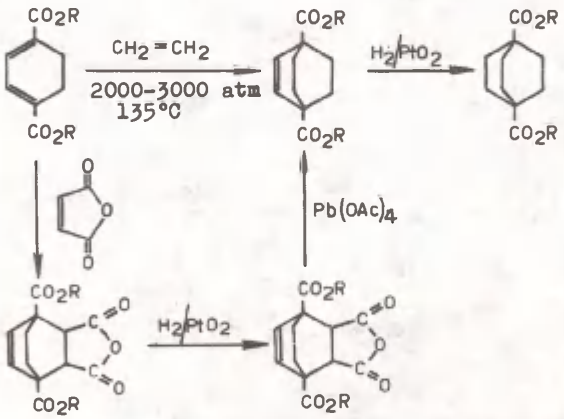


Some other synthetic methods are also suggested[12-15]. Among the three series of disubstituted derivatives the methods of synthesis for the series of 1-Y-4-X have been studied the most completely. Synthesis of these compounds is laborious and involves several steps. Schemes 1 and 2 [7,16] illustrate the main routes of synthesis in general outline.

Scheme I



Scheme 2



As one can see from these schemes diethylbicyclo[2.2.2] octane - 1,4 - dicarboxylate is obtained either through the salts of cyclic di-β-ketoesters [7,8,17-21] (scheme 1) or by the Diels-Alder reaction [5,6,16,22-25] (scheme 2). In the hydrolysis of the product obtained ethylbicyclo[2.2.2]octane--1,4-dicarboxylate is formed. The latter is an initial compound to synthesize other derivatives of this series by the techniques of Roberts [7] and Holtz [8].

For the synthesis by the Diels-Alder reaction derivatives of 1,3-cyclohexadiene (whose synthesis also involves some steps [26-28]) play the role of the initial diene.

Literature date about methods of synthesis of representatives of other two series are more scanty. In most cases the diene synthesis is used.

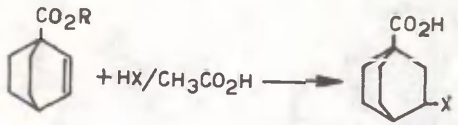
Synthesis of derivatives where Y=X=CO_2R or CO_2H [6,22,25] has been carried out more successfully. Much less advances have been made with the synthesis at X≠Y. Introduction of the substituent with X = Br, $COCH_3$, CHO, and CN at Y = = CO_2H or CO_2R is described only[23-25,29].

Table 1 summarizes the information about methods of synthesis of the 1-Y-2-X derivatives.

As one can see from this table the mixture of 1,2- and 1,3-isomers is often formed, 1,2- isomer prevailing in the mixture. Separation of these isomers generates additional difficulties and has been made only in some cases[6,22,29].

One of the possible ways to obtain 1,3-isomers is to isolate them from their mixtures with 1,2-isomer.

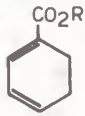
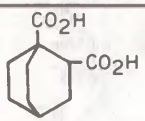
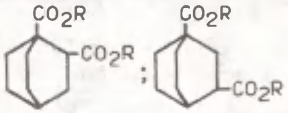
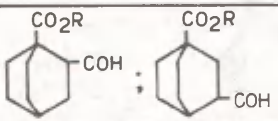
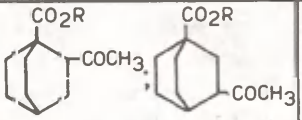
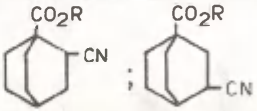
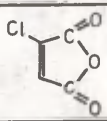
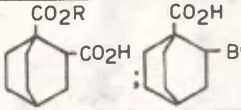
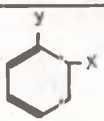
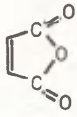
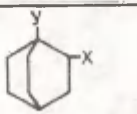
Besides, to obtain 1,3-carboxyhalogenobicyclo [2.2.2] octane the following method has been suggested[23,29]:



R = C_2H_5 or H
X = Br, Cl, J

Table 1

Methods of Synthesis of the Derivatives of the 1-Y-2-X Series

Diene	Dienophile	End-Products	Refs
 R = CH_3 or C_2H_5	$H_2C{=}CHCO_2H$		22
	$H_2C{=}CHCO_2R$	 4:1	6 22
	$H_2C{=}CHO$		24
	$H_2C{=}CHCOCH_3$	 4:1	25
	$H_2C{=}CHCN$	 .3,5:1	29
			22 23
		 y=x=CO_2R or CO_2H	6

From this brief review one can see the necessity to thoroughly verify and elaborate methods of synthesis of the stated types of bicyclo [2.2.2] octane disubstituted derivatives.

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STUDY OF REACTIVITY OF SUBSTITUTED BICYCLO[2.2.2] OCTANES. 2.Verifying Methods to Obtain Diethyl-2,5-dioxobicyclo[2.2.2]octane-1,4-dicarboxylate*

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Literature methods of synthesis of diethyl-2,5-dioxobicyclo [2.2.2] octane--1,4-dicarboxylate (II) are verified and specified.

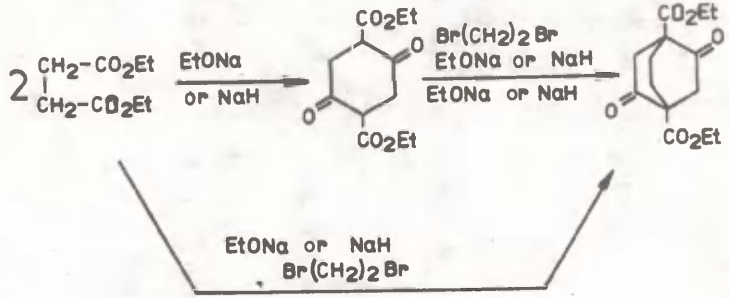
The products obtained are characterized by m.p., UV and IR spectra; the degree of their purity was checked with the use of thin-layer chromatography.

Synthesis of II was performed according to the modified procedure of Guha.

Diethyl-2,5-dioxobicyclo [2.2.2] octane -1,4-dicarboxylate (II) is an important intermediate for one of possible methods of synthesis of 1.4-disubstituted derivatives of bicyclo [2.2.2] octane [1-5].

To obtain this product diethyl succinate is used as an initial compound. Through the process of Dieckmann condensation it is influenced by the condensing agent C_2H_5ONa or NaH to yield 2,5-dioxo-1,4-dicarboethoxycyclohexane (I). The skeleton of bicyclooctane is formed by bridging disodium salt of the intermediate (I) with ethylene dibromide (see the scheme).

* For Comm.1 see Ref. 1.



Since in the Dieckmann reaction 2,5-dioxo-2,4-dicarboethoxycyclohexane is formed in the form of sodium salt, some authors have obtained compound II via one-step process without isolating intermediate I (see the scheme).

With isolation of intermediate I higher yields of II (59[4] and 80%) over those in one-step process (32[2] and 40%) are obtained. Besides, in the first case the end-product is characterized by m.p. 112°C[4] (cf. with 108-110°C[2] or 109-111°C[3] in the second case).

The present work reports the results of comparative study of the two synthetic methods.

Experimental

The degree of purity of the product obtained was checked with the use of thin-layer chromatography (TLC): adsorbent - silica gel - finished plates for chromatography in thin layers "Silufol" (firm "Kavalier", Czechoslovakia). The mixture of benzene with ethyl acetate (95:5) or with petroleum ether (3:1 v/v) was used as eluents.

To detect chromatographic spots UV radiation source OLD-41 with nominal wavelength 254 nm was used. The ester was identified in the form of hydroxanic acids [6,7].

UV spectra were registered on a "Hitachi" EPS-3T spectrometer in ethyl alcohol.

IR spectra were registered on a "Spectromom-2000" spectrometer.

Diethyl ester of succinic acid (grade "Pure for analysis") was dried over anhydrous $MgSO_4$ and used freshly distilled. B.p. 86°C (6 mm Hg).

1,2-Dibromoethane (grade "Pure for analysis") was dried over anhydrous $CaCl_2$ and distilled in vacuum. B.p. 58.5°C (60 mm Hg).

Ethyl alcohol ("rectificate") was treated with solid NaOH ("chemically pure"), distilled, dried by boiling over freshly calcinated CaO and redistilled. Pinal dehydrating was done by the Lund-Bjerrum method[8]. Then rectification was carried out and the mean fraction was collected.

2,5-Dioxo-1,4-dicarboethoxycyclohexane (I) was synthesized by the Nielsen-Carpenter procedure [9] in the atmosphere of dry argon purified from O_2 [10], yield 69-71%, m.p.=127.5--128.0°C (lit.[9] yield 64-68%, m.p.=126-128°C).

TLC has indicated the presence of one component with R_x=0.83 only (eluent, benzene-ethyl acetate) or R_x=0.31 (benzene-petroleum ether).

In UV spectrum of the product maximum at 244 nm was found ($\mathcal{E}$ =1.39 . 10^4).

In IR spectrum the absorption band at 1630 cm^{-1} (characteristic of the C=O group) was observed.

Diethoxy-2,5-dioxobicyclo [2.2.2] octane-1,4-dicarboxylate (II) was first synthesized by the procedure of Roberts[2], the yield was 28-30%, m.p.=106-115°C.

TLC has indicated that the product contains 8-10 different substances. Two among them (with the values of R_x= 0 and $R_x \approx 60$) were identified as esters.

The UV spectrum of this product was of complex character. After purifying by the procedure [2] the number of compounds

decreased to 3-4, m.p.=108-118°C.

To synthesize II somewhat modified procedure of Guha[4] was used. The reaction was carried out in the atmosphere of dry argon purified from O_2. The system was protected from moisture.

In one liter flask from 300 ml of anhydrous alcohol and 7.2 g (0.32 g - atom) of fine-cut sodium the alcoholate was prepared. Then 40 g (0.43g-mole) of compound (I) was added to it and the mixture was heated for 2-3 hours at 90°C. Alcohol was distilled in the atmosphere of argon. To remove the last traces of alcohol the flask was heated for 1-2 hours at 150°C at the pressure of 7 Torr. To dry disodium compound 200 ml of dry dibromoethane was added and, energetically mixing, heated at 120°C. The reaction was believed to be completed when reaching neutral pH which required 26-40 hours. Non-reacted 1,2-dibromoethane was distilled with steam. When cooling, a yellow crystal precipitate fell out. After recrystallizing the product from ethyl alcohol and treating the precipitate with 1% solution of NaOH 26.5 - 28g (61-63%)* the white crystal product (m.p. 111.8-112°C) was obtained.

After distilling 1,2-dibromoethane the obtained crude product contained 3-4 components (according to the TLC data). After purifying it contained only one component with $R_x = 0$ which was identified as the ester.

UV spectrum had the absorption maximum at 203 nm ($\varepsilon = 7.4 \cdot 10^2$).

IR spectrum had the band characteristic of an ester (1720 cm^{-1}).

Results and Discussion

From the above data one can see that the synthesis without isolating and purifying intermediate I produces a complex mixture of products and hardly can be used for

* It should be noted that according to Refs. 5 and 11 the higher yield can be obtained if using NaH as condensing agent. Unfortunately, under our conditions this procedure is unapplicable due to inaccessibility of NaH.

preparative production of needed product II.

At the same time the described procedure of synthesis involving the intermediate isolation of compound I has proved to be applicable, since the yield of the pure product is high enough, more than 60%.

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STUDY OF REACTIVITY OF SUBSTITUTED BICYCLO [2.2.2] OCTANES

3. Influence of Reaction Conditions on Absolute and Relative Yields of Diethyl Eetere of Bicyclo [2.2.2] octane-1,2- and 1,3-Dicarboxylic Acids*

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Influence of temperature and reaction conditions on the absolute and relative yields of diethyl eetere of bicyclo [2.2.2] octane-1,2- and 1,3-dicarboxylic acids waa studied. The procedure of GLC was used. Optimum conditions of synthesis are determined.

Possible methods to produce 1-Y-2-X and 1-Y-3-X derivatives of bicyclo [2.2.2] octane where Y = COOH or COOR were considered in Ref. 1.

There is little information about eynthesis of derivatives with X = CO_2R, CO_2H, Br, COH, $COCH_3$, and CN [3-6,13].

To obtain bicyclo[2.2.2] octane derivatives diene synthesis with subsequent hydrogenation of adduct is applied most often. The reaction is carried out by heating either in flask with reflux condenser [3-4,7-9] or in sealed ampules [5,13] at 100-150°C or higher temperatures. The mixture of 1,2- and 1,3-isomers is formed, the total yield being 50-80% [7-8,13]. In all cases 1,2-isomer is mainly formed with some amount of 1,3-isomer [3,7-8,13].

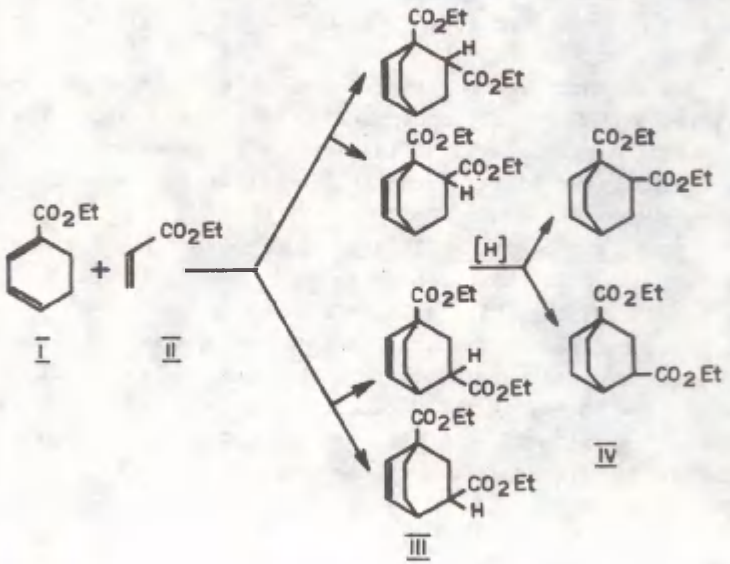
Influence of temperature and reaction conditions on the absolute and relative yields of these isomers has not been studied in detail, though literature presents some contra-

* For communications 1 and 2 see Refs. 1 and 2

dicting data on condensation products of 1-substituted dienes[7,10].

The purpose of this work is to specify the optimum conditions of diene condensation and mixture composition of 1,2- and 1,3-isomers of bicyclo [2.2.2] octane at $Y=X=CO_2Et$.

The synthesis was done by the literature procedure [3]:



We have studied the total yield of the mixture of products (III) and also amounts of 1,2- and 1,3-isomers in mixture (IV) obtained after hydrogenating intermediate (III) on PtO_2 in the atmosphere of hydrogen (at atmospheric pressure).

Experimental

Ethyl ester of 1,3-cyclohexadiene carboxylic acid (I) was synthesized by the procedure of Grob and Ohta [11], b.p.= = 92-94°C (12 mm Hg, n_D^{25} = 1.4978 (Lit.[11] b.p.= 90-92°C (11 mm Hg)).

UV spectrum of diene was registered on a "Hitachi" EPS-3T spectrophotometer in ethyl alcohol and had the maximum at 292 nm (ε =8.13 . 10^3). (Lit.[3] λ_{max} = 292 nm, ε = = 8.26 . 10^3).

IR spectrum was registered in a thin layer between the plates of HaCl on a "Spectromom"-2000 spectrometer. The absorption maxima at 1710 and 1635 cm^{-1} characteristic of the conjugated ester group and double bond, respectively, were observed.

Ethyl ester of acrylic acid (II)(grade "Pure for analysis") was dried over anhydrous $MgSO_4$ and used freshly distilled only, b.p.=99.0 – 99.5°C/760 mm Hg.

The content of isomers was determined with GLC, using "Vŏruchrom" A-1 chromatograph with column 3m x 2 mm filled with XE - 60(5%) at 200°C (according to the literature data the column with DS - 550 was used for analogous purpose[3]). The per cent composition of the mixture was calculated by the formula:

$$\% A = \frac{\text{area of peak A}}{\text{total area of peaks}} \cdot 100$$

Areas of peaks were considered as equalled to the product of the peak height and its halfwidth [9].

The mixture of products of runs 3 and 4 is characterized by the NMR-^{13}C spectrum with the use of a Bruker spectrometer. Tetramethylsilane was used as an internal standard

and deuterated acetone as a solvent*.

According to the spectrum obtained the ratio of 1,2- and 1,3 isomers was 3:1.

Table 1 summarizes the data on synthesis.

Table 1

Data on the Syntheses by the Scheme. Procedure A, heating with reflux condenser in the atmosphere of anhydrous argon. Procedure B, heating in the sealed ampule in the atmosphere of anhydrous argon. The reaction mixture occupied 1/3 of the ampule volume.

NN	Amount of diene (I) and dienophile (II) in g (in moles)	Reaction conditions	b.p.°C of the mixture (III)	Yield (III) %	Ratio of 1,2- and 1,3- -isomers in the mixture (IV)**
***	5,0 (0.033) (I) 9.8 (0.098) (II)	Refluxing 24 h., temp. is not pointed out	110-113° 0.07mm Hg	50.0	3.8 : 1
1	5.0 (0.033) (I) 9.8 (0.098) (II)	Proc.A,24 h. 115°C	152-155° 4 mm Hg	49,6	4.1 : 1
2	3.7 (0.024) (I) 6.5 (0.065) (II)	Proc.B,23 h. 115°C	149-150° 3 mm Hg	66.0	4.7 : 1
3	3.5 (0.023) (I) 6.7 (0.067) (II)	Proc.B,18 h. 140°C	156-160° 5 mm Hg	71.0	3.0 : 1
4	3.0 (0.019) (I) 8.0 (0.08) (II)	Proc.B,18 h. 140°C	155-160° 5 mm Hg	74.0	3.0 : 1
5	3.0 (0.019) (I) 8.0 (0.08) (II)	Proc.B,13 h. 155°C	149-152° 3 mm Hg	76.0	2.8 : 1

* The authors are grateful to T. Pehk (Institute of Cybernetics) for recording this spectrum.

** The hydrogenation of mixture (III) proceeded with the yield about 85%,b.p. of the mixture obtained (IV) was 149 - 149.5°C/2 mm Hg

*** From Ref. 3.

Results and Discussion

From the data obtained one can see that the yield of the mixture of products (III) is increased approximately by 15% with the reaction being carried out in the sealed ampule (cf. runs 1 and 2). The optimum temperature for the synthesis of these compounds is 140°C. At the higher temperature (155°C) the amount of resinous side product is increased. Over the temperature range studied there is a slight dependence of 1,2- and 1,3-isomer on the temperature. At the higher temperature the relative yield of 1,3-isomer is somewhat increased.

Synthesis in the sealed ampule at 140°C is the most expedient.

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NMR Spectra of Acetylenes $R_1C{\equiv}CR_2$. Structural Effects of Groups R_1 and R_2 on $^{13}C_{sp}$ Shifts

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A correlation analysis of ^{13}C chemical shifts δ of C_{ap} atom for a large series of mono- and disubstituted acetylenes $R_1C{\equiv}CR_2$ has been carried out. The structural effects of various groups R_1 and R_2 on the value of δ are found to be independent and may be fairly described within the axiomatics of the polylinearity principle and the LFER principle. These effects are linear combinations of inductive, steric, and resonance contributions.

Additivity in the structural effects of different substituents on the shielding of the aromatic ring ^{13}C nuclei is a wide-spread conception in the ^{13}C NMR spectroscopy of polysubstituted benzenes (e.g. see Refe.1 and 2).However, recent results show unambiguously considerable differences between the measured ^{13}C chemical shift values $\delta^{13}C$ and those calculated within additive approach for a large number of 1,4-disubstituted benzenes[3-7], although a physical nature of this non-additivity is not fairly realized up to now. One may obviously assume that in disubstituted acetylenes $R_1C{\equiv}CR_2$, these compounds as well as 1,4-disubstituted benzenes and trans-1,2-disubstituted ethylenes are the simplest unsaturated disubstituted compounds whose substituents do not interact sterically, the effects of groups R_1 and R_2 on the triple carbon bond shielding are also non-additive. A vast body of data on NMR ^{13}C spectroscopy is now accumulated for disubstituted acetylenes $R_1C{\equiv}CR_2$ (see Appendix II). Chemical shifts $\delta^{13}C$ in these compounds are found to depend strongly on structure of R_1 and R_2. When variations in structure of group R_1(or R_2) are small, e.g. the group

is m,p-substituted phenyl, this dependence is described satisfactorily by the corresponding substituent constants[7]. However, more general relationships covering up not only a wide variation in the structure of one of the groups R_1 and R_2, but their simultaneous variations are not known. We have attempted here to construct such relationship in terms of the polylinear principle (PPL)[8-10]. It has been used successfully to describe quantitatively the combined effect of several factors on different properties of organic compounds[9-14]. One of us has shown previously[14] that PPL well describes the non-additivity in the effects of groups R_1 and R_2 on $\delta^{13}C$ of the ring carbon at R_1 in 1,4-$R_1ØR_2$ and explains the observed isoparametricity phenomenon[14,15], i.e. a reversal of the effect of R_1 on the $\delta^{13}C$ value with a change in structure of the substituent R_2.

Denoting the substituent at the atom-detector of the ^{13}C signal in compounds $R_1C{\equiv}CR_2$ as R_1, we assume then that formal brutto-mechanism for the effect of various groups $R_1(R_2)$ on the $\delta^{13}C$ of the nucleus under consideration is the same and independent of the nature of the group $R_2(R_1)$. In such a case, the $\delta^{13}C$ value may be given, according to the PPL, as follows:

$$\delta(R_1C{\equiv}CR_2) = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 \qquad (1)$$

Here X_1 and X_2 are the scales (measures) for structural effects of groups R_1 and R_2, respectively; a_0+a_{12} coefficients, a_{12} does not equal zero when the effects of R_I and R_2 are non-additive. The coefficients of equation (1) should obey the conditions[8-10]: $a_0 = \delta(R_1^oC{\equiv}CR_2^o)$ and $a_1 = a_2 = 1$, when, in accordance with PPL, X_1 and X_2 are defined as the differences:

$$X_1 = \delta(R_1C{\equiv}OR_2^o) - \delta(R_1^oC{\equiv}CK_2^o) \qquad (2)$$

$$X_2 = \delta(R_1^oC{\equiv}CR_2) - \delta(R_1^oC{\equiv}CR_2^o) \qquad (3)$$

Here R_1^o and R_2^o are some substituents R_1 and R_2 taken arbitrarily as standard ones. Let us take $R_1^o = R_2^o = H$, since the $\delta^{13}C$ values are known for a great number of monosubstituted

acetylenes. The X_1 and X_2 values calculated in this way for different substituents R_1 and R_2 are enlisted in Appendix I.The absence of correlation between these measures shows that the nature of effects of groups R_1 and R_2 on the $\delta^{13}C_{sp}$ values for $R_1C{\equiv}CR_2$ is different*.

The necessary and sufficient condition for the equation (1) applicability is the applicability of the LFER principle to $\delta^{13}C$ of $R_1C{\equiv}CR_2$, i.e. the $\delta^{13}C$ values for any two series of the compounds with varying groups R_1(or R_2) and fixed at different levels groups R_2(or R_1) should be linearly related; that is, for any R_1 and R_2 described by equation (1), the relations

$$\delta^{13}C(R_1C{\equiv}CR_2)_{R_2=const} = A + B\delta^{13}C(R_1C{\equiv}CH) \qquad (4)$$

$$\delta^{13}C(R_1C{\equiv}CR_2)_{R_1=const} = C + D\delta^{13}C(HC{\equiv}CR_2) \qquad (5)$$

should be observed in experiment.

Equations (4) and (5) have been verified on the data for 40 groups R_1 and 38 groups R_2. The mean standard deviations and coefficients of correlations ($\bar{s}_1$ = 1.33 ∓ 0.15, $\bar{s}_2$ = 1.17 ∓ 0.14, $\bar{r}_1$ = 0.985 ∓ 0.004 and $\bar{r}_2$ = 0.986 ∓ 0.004; the averaged numbers $\bar{n}_1$ and $\bar{n}_2$ of points in the sets are as large as 6 and 7) for these correlations show a fair applicability of the LFER principle to structural effects of groups R_1 and R_2 on the property of interest. The slopes B and D in these correlations are found to be practically independent of the nature of groups R_2 and R_1 respectively. These slopes are nearly equal to 1.00, i.e. $\bar{B}$ = 0.999 ∓ 0.027, $\bar{D}$ = 0.978 ∓ 0.028. The correlations found for certain groups R_1 and R_2 are given in Table 1.

Thus, the $\delta^{13}C_{sp}$ dependence on the structure of R_1 and

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*Substituents R_1 and R_2 may affect the $\delta^{13}C$ value in different mechanisms.But if the number and types of these more fundamental mechanisms are the same for both substituents, their partial contributions to the general effects of these substituents may differ substantially; see below.

Table 1

Coefficients and Statistics of Equations (4) and (5) for Some Sets of Disubstituted Acetylenes

Subetituent	A or C	B or D	n[a]	r[b]	s[c]
$R_1 = CH_3$	0.5∓3.1	0.94∓0.04	24	0.989	1.15
$R_1 = Ph$	4.6∓3.2	1.02∓0.04	14	0.991	1.36
$R_1 = Si(CH_3)_3$	16.9∓4.3	1.06∓0.05	12	0.992	1.06
$R_2 = CH_3$	3.4∓1.5	1.06∓0.02	23	0.997	1.03
$R_2=C(OH)(CH_3)_2$	19.3∓1.7	0.97∓0.02	14	0.996	1.31
$R_2 = Si(CH_3)_3$	12.7∓2.1	1.05∓0.03	14	0.996	1.70

[a]The number of points in the set. [b]Coefficient of correlation. [c]Standard deviation for the regression.

R_2 in compounds $R_1C{\equiv}CR_2$ should be described by equation (1) with an accuracy at least similar to that found for correlations within equations (4) and (5). According to Table 2, the $\delta^{13}C$ values for acetylene itself and for 46 its derivatives with alkyl or electronegative aliphatic* groups R_1 and R_2 are, in fact, well described by this equation (Reg. A.1). Exclusion of four points with significant deviations increases the description quality (Reg. A.2). The coefficients a_0, a_1, a_2 in these regressions do not differ from their theoretical values (72.0, 1.00, and 1.00, respectively), although the a_2 value has large uncertainty. On the other hand, the estimate of a_{12} is statistically insignificant and, as a result, exclusion of the term $a_{12}X_1X_2$ does not affect the regression quality (see Reg.B.1 and B.2)at the better convergence of the estimate for coefficient a_2. Thus, one can conclude that the structural effects of groups R_1 and R_2 on the $\delta^{13}C_{sp}$ values for disubstituted acetylenes are independent. This

*Substituents of type $X_1X_2X_3C(CH_2)_n$, $X_1X_2HC(CH_2)_n$ or $XH_2C(CH_2)_n$, where n = 0,1,2,... and $X_1 \div X_3$ are electronegative substituents of the type Cl, Ph, NO_2, etc.

Table 2

Coefficients and Statistics of Equation (1)

Reg.	a_0[a]	a_1	a_2	a_{12}	n[b]	R[c]	S[d]
A.1	71.240∓ 0.56	1.050∓ 0.055	0.931∓ 0.144	0.005∓ 0.013	47	0.980	0.94
A.2	71.080∓ 0.419	1.085∓ 0.042	0.889∓ 0.108	0.012∓ 0.010	43[e]	0.990	0.70
B.1	71.395∓ 0.388	1.034∓ 0.034	0.984∓ 0.048		47	0.980	0.94
B.2	71.523∓ 0.265	1.024∓ 0.024	0.975∓ 0.036		42[f]	0.990	0.63
C.1	72.342∓ 0.292	0.955∓ 0.027	0.941∓ 0.032	0.006∓ 0.002	225	0.988	2.25
C.2	72.531∓ 0.191	0.957∓ 0.018	0.962∓ 0.022	0.005∓ 0.002	195[g]	0.994	1.49
D.1	72.089∓ 0.275	0.971∓ 0.026	1.014∓ 0.011		225	0.988	2.28
D.2	72.386∓ 0.183	0.970∓ 0.018	1.014∓ 0.009		196[h]	0.994	1.50

[a]The "theoretical" value for a_0 is 72.00; see the text. [b]The number of points in the set. [c]Coefficient of multiple correlation. [d]The regression standard. [e]Without significantly deviated points for compounds 5-7, 6-7, 15-15, 15-44. [f]Points for compounds 5-7, 6-7, 15-15, 15-44, 51-44. are ruled out because of their significant deviations for the regression found. [g]Without significantly deviated points for compounds 136-7, 141-7, 108-3, 141-5, 127-10, 15-50, 50-15, 39-108, 108-39, 54-39, 136-46, 136-45, 127-46, 54-141, 127-57, 105-105, 105-127, 107-127, 128-127, 135-128, 128-135, 141-136, 141-108, 90-118, 81-118, 88-118, 94-118, 84-118, 81-103, 15-142. [h]The points for compounds 136-7, 141-7, 108-3, 141-5, 15-50, 50-15, 39-108, 108-39, 54-39, 136-46, 136-45, 127-57, 105-105, 105-127, 107-127, 128-127, 133-108, 135-128, 128-135, 141-136, 141-108, 90-118, 81-118, 88-118, 94-118, 84-118, 81-103, 15-142 are excluded due to their significant deviations. Substituents R_1 and R_2 in the compounds $R_1C{\equiv}CR_2$ are here denoted by numbers corresponding to those in Appendix I.

conclusion is confirmed by the independence of B and D in equations (4) and (5) on the nature of groups R_2 and R_I, respectively. Similar additivity is also observed for the effects of groups R_1 and R_2 on the ring carbon shifts in 1,3-disubstituted benzenes whereas the substituent effects in their 1,4-isomers are significantly non-additive[3,4,14]. It should be noted that regressions A and B in Table 2 have lower standard deviations than those found for equations (4) and (5) (Table 1).

Substituents R_1 and R_2 covered by regressions A and B (Table 2) are unable to all types of resonance interaction, but hyperconjugation which seems to be negligible in the ground state of organic compounds[9,17]. Addition of the data for 178 other disubstituted acetylenes* with groups R_1 and R_2 being able to resonance effects (COX, OR, SR, X or $MX_1X_2X_3$, with M = Si, Ge, Sn) decreases dramatically the regression accuracy (Regs. C.1 and D.1). When a number of significantly deviating points is excluded, the regression quality increases considerally (Regs. C.2 and D.2). An actual absence of the cross-term in equation (1) is confirmed by similarity in the values of statistics S and R for Regs. C.2 and D.2, and by close resemblance of the $a_0 + a_2$ values in the latter regression to their "theoretical" values. Worse regression standard for Regs. C.2 and D.2 than those found for A.2 and B.2 may be due to the presence in the added disubstituted compounds of additional mechanisms, governing the substituent effects on the $\delta^{13}C$ value, which are absent in the corresponding monosubstituted compounds and in those described by regressions A.2 and C.2. Solvation effects and uncertainties related with the use of the data of different authors may also decrease the accuracy of these regressions.

The absence of the cross-term in equation (1) requires

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*All monosubstituted compounds except acetylene and its methyl and ethyl derivatives were not included in this set.

that the $\delta^{13}C$ values for disubstituted and corresponding monosubstituted acetylenes should obey a simple relationship:

$$\delta(R_1C{\equiv}CR_2) = a_0 + a_1\left[\delta(R_1C{\equiv}CH) + \delta(HC{\equiv}CR_2)\right] \quad (6)$$

Here a_0 and a_1 should be the $\delta^{13}C$ value for acetylene with the opposite sign and 1.00 respectively. Fig.1 shows the corresponding theoretical relationship between $\delta(R_1C{\equiv}CR_2)$ and $\delta(R_1C{\equiv}CH) + \delta(HC{\equiv}CR_2)$ and fit of experimental points for 229 compounds (226 are disubstituted ones) to this relationship. For 185 points the values $\Delta = \delta^{13}C_{exp.} - \delta^{13}C_{calc.}$ do not exceed ± 2 ppm. Among the remained 44 points $\Delta \geqslant 4$ only for 14 points. The lowest deviations are observed for the compounds with alkyl and electronegative aliphatic groups R_1 and R_2. The deviations for other compounds are rather unsystematic. It may be noted here that those are positive for many compounds with aryl or α,β -unsaturated groups R_1 and/or R_2, whereas a lot of compounds with $R_1 = MX_1X_2X_3$ (M = Si, Ge, Sn) have negative Δ values. For compounds of the latter type the maximum deviations are observed. With $R_2 = MX_1X_2X_3$ the values of Δ are low and unsystematic.

Table 3 shows the coefficients and statistics for equation (6) and for its extended form, i.e. equation (7)*, which considers some of above features in deviations for various groups of substituents.

$$\delta(R_1C{\equiv}CR_2) = a_0 + a_1\left[\delta(R_1C{\equiv}CH) + \delta(RC{\equiv}CR_2)\right] + a_2n_{Ar} + a_3n_{\pi} + a_4n_M \quad (7)$$

Here n_{Ar} is the number of aryl groups R_1 and/or R_2, n_{π} is

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* The analysis of deviations observed in Fig. 1 allows us to assume that (i) the coefficients a_2 and a_3 do not depend, at the first approximation, on the position of group R_1 or R_2 or on the nature of substituents in aryl- or α,β-unsaturated group, (ii) the coefficient a_4 does not depend on the nature of substituents X_1, X_2 and X_3 in groups $R = MX_1X_2X_3$.

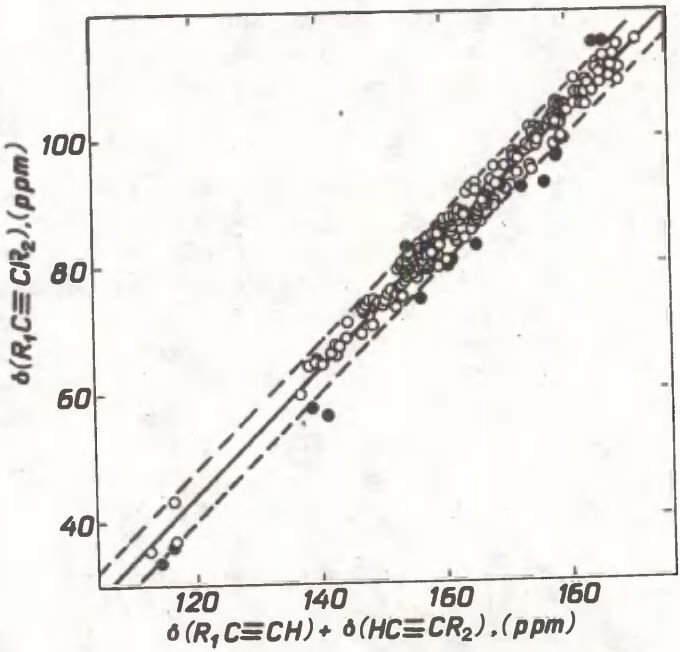

Fig.1. Relationship between $\delta^{13}C$ for disubstituted acetylenes $R_1C{\equiv}CR_2$ and the sum $\delta(R_1C{\equiv}CH) + \delta(HC{\equiv}CR_2)$ for corresponding monosubstituted compounds. The dashed lines form the ∓4ppm "corridor" for the line with theoretical intercept and slope; see the text. The shaded circles correspond to $\Delta \geqslant$ ∓4ppm.

Table 3

Coefficients and Statistics of Equations (6) and (7)

Reg.	a_0	a_1	a_2	a_3	a_4	n[a]	R[a]	S[a]
E.1	-75.136∓ 4.718	1.019∓ 0.031				47[b]	0.980	0.94
E.2	-74.134∓ 3.519	1.013∓ 0.023				42[c]	0.990	0.64
F.1	-73.529∓ 1.636	1.009∓ 0.010				228[d]	0.988	2.22
F.2	-71.252∓ 1.137	0.997∓ 0.007				195[e]	0.995	1.39
G.1	-73.564∓ 1.792	1.011∓ 0.011	-0.372∓ 0.402		-1.108∓ 0.411	229[f]	0.986	2.42
G.2	-75.564∓ 1.208	1.021∓ 0.008	0.475∓ 0.264		-1.335∓ 0.268	201[g]	0.994	1.47
H.1	-73.651∓ 1.796	1.011∓ 0.011		0.155∓ 0.361	-0.995∓ 0.419	229[f]	0.987	2.42
H.2	-75.430∓ 1.157	1.022∓ 0.007		0.929∓ 0.223	-1.162∓ 0.260	199[h]	0.995	1.40
I.1	-73.610∓ 1.790	1.011∓ 0.011			-1.041∓ 0.404	229[f]	0.986	2.42
I.2	-74.775∓ 1.219	1.020∓ 0.008			-1.376∓ 0.269	206[i]	0.994	1.49
J.1	-66.444∓ 2.016	0.965∓ 0.013				144[j]	0.987	1.73
J.2	-71.321∓ 1.662	0.998∓ 0.011				130[jk]	0.992	1.31
K.1	-66.726∓ 2.045	0.967∓ 0.013	-0.277∓ 0.330			144[j]	0.987	1.73
K.2	-71.406∓ 1.627	0.998∓ 0.011	0.564∓ 0.264			129[jl]	0.993	1.28
L.1	-65.775∓ 2.067	0.959∓ 0.014		0.419∓ 0.304		144[j]	0.987	1.73
L.2	-69.961∓	0.986∓		1.121∓		129[jm]	0.994	1.19

[a] n, R, and S have the same meaning as those used in Table 2. [b] For acetylenes with substituents R_1 and R_2 unable to reasonable interactions. [c] The points for compounds 5-7, 6-7, 15-15, 15-44, 51-44 are excluded because of significant deviations. [d] For all disubstituted compounds, except ~~127~~-107. [e] When significantly deviated points for com-

pounds 136-7, 141-7, 141-5, 127-10, 15-50, 50-15, 108-39, 54-39, 127-15, 136-46, 136-45, 127-46, 54-115, 54-141, 105-105, 105-127, 107-127, 127-108, 128-127, 135-108, 135-128, 128-135, 141-136, 141-108, 90-118, 81-118, 94-118, 84-118, 81-103, 88-118, 15-142 have been ruled out. [f]For all compounds. [g]Significantly deviated points for 141-7, 15-50, 50-15, 39-108, 108-39, 54-39, 136-46, 96-105, 105-105, 105-127, 127-107, 107-127, 128-127, 135-128, 128-135, 141-136, 141-108, 90-118, 81-118, 88-118, 94-118, 84-118, 81-103, 15-142 are excluded. [h]Without the points listed in foot-note for Reg. G.2 as well as points 135-108, 54-115, 100-105. [i]Significantly deviated points for compounds 141-7, 39-108, 108-39, 54-39, 105-105, 105-127, 135-128, 141-136, 141-108, 81-118, 88-118, 84-118, 81-103, 15-142 are excluded. [j]For all compounds without the groups R_1, $R_2 = MX_1X_2X_3$, M = Si, Ge or Sn. [k]The points for compounds 15-15, 108-39, 54-39, 54-115, 96-105, 105-105, 90-118, 81-118, 88-118, 94-118, 84-118, 81-103, 150-81, 15-142 are omitted because of significant deviations. [l]The same points as those in the case of Reg. J.2 and point for 100-105 are excluded because of significant deviations. [m]Without significantly deviated points for compounds 108-3, 108-39, 54-39, 54-115, 96-105, 100-105, 105-105, 90-118, 81-118, 88-118, 94-118, 84-118, 81-103, 150-81, 15-142. All compounds mentioned are denoted in the same way as that used in Table 2.

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the number of aryl and/or α,β-unsaturated groups R_1 and/or R_2 in compounds $R_1C{=}CR_2$ (n_{Ar}, $n_{\pi} = 0,1,2$), $n_M = 1$ when substituent $MX_1X_2X_3$ is in position R_1; $a_2 \div a_4$ are additional contributions due to the presence of corresponding groups. Corresponding to equation (6) regression (E.1 and E.2) for compounds with groups R_1 and R_2 (unable to conjugation) displays fair statistical standard and a_0, a_1 values close to theoretical ones. Inclusion of compounds with other groups R_I and/or R_2 worsens sharply the regression qual-

ity (Reg. F.1). However, exclusion of a number of markedly deviated points increases the regression accuracy (Reg. F.2). The estimates for a_0 and a_1 in regression F.2 also agree well with their "theoretical" values. Further improvement in the regression quality by means of exclusion of other points with significant but small deviations is senceless, since the accuracy found for LFER principle applicability to $\delta(R_1C{\equiv}CR_2)$ does not exceed ∓1.3 ppm (see above, $\bar{s}$ = 1.3 ∓ 0.2). This is also true for all other regressions in Table 3. Extention of equation (6) by terms a_2n_{Ar} and a_4n_M does not improve its quality (Reg. G.1 and G.2) and leads to insignificant estimate for a_2. Additions of term a_3n_π and a_4n_M or a_4n_M also produce no considerable effect although both a_3 and a_4 are significant. Regs. G.2, H.2, I.2 show some discrepancy between their estimates for a_0, whereas a_1 values are in good agreement. Exclusion of the data for all compounds with $R_1 = MX_1X_2X_3$ (M = Si, Ge or Sn) leads to a good correlation by equation (6) (Reg. J.2). Addition of terms a_2n_{Ar} or a_3n in this equation is also not effective in this case and the estimate for a_2 is insignificant. Thus, within discussed experimental data any refinement of equation (6) appears to be meaningless. The scattering of exsperimental data around the theoretical line in Fig.1 seems to be mainly due to the fact that the data used are from different sources and may be caused by difference in solvation, concentration and by other purely experimental reasons, e.g. the use of different internal and external standards and solvents. All these reasons are not connected with the electronic effects of groups R_1 and R_2 on the $\delta^{13}C$ values. Hence, the terms related with coefficients $a_2 \div a_4$ in equation (7) may be only artefacts. At any rate, their reliability requires more thorough investigation.

It is obvious that substituents R_1 and R_2 affect the $\delta^{13}C_{sp}$ value by several mechanisms simultaneously. Fair applicability of equations (1), (6) and particularly of

Table 4

The Results of Regression Analysis of Scales X_1 and X_2 in Framework of Equation (8)[a].

Reg.	X	a_0	a_1	a_2	a_3	n	R	S
M.1	X_1	18.778± 0.519	-4.286± 0.470	-3.888± 0.258		34	0.949	1.206[b]
M.2		19.361± 0.353	-4.928± 0.323	-4.032± 0.171		30	0.981	0.771[b,c]
N.1		18.741± 0.442	-4.230± 0.388	-3.884± 0.233	-4.816± 0.471	46	0.949	1.045[d]
N.2		19.196± 0.264	-4.978± 0.227	-3.928± 0.132	-4.747± 0.263	39	0.986	0.557[d,e]
O.1	X_2	-2.991± 0.882	5.058 ± 0.800	0.732± 0.438		35	0.754	2.049[b,f]
O.2		-3.976± 0.411	7.077± 0.427	0.719± 0.212		27	0.961	0.802[b,f,g]
P.1		-3.288± 0.775	5.418± 0.680	0.755± 0.391	4.979± 0.825	46	0.862	1.853[d,f]
P.2		-4.111± 0.366	7.331± 0.360	0.717± 0.194	4.524± 0.390	39	0.977	0.786[d,f,g]

[a] n, R, and S have the same meaning as those in Table 2and 3. Constants δ^* for vinyl and electronegative aliphatic groups are from Refs. 25 and 26 or are estimated on the basis of $Z_C^* = 0.36$. For aryl groups δ^* are calculated as it has been described in Ref. 18. [b] For alkyl and electronegative aliphatic groups but without the point for H. [c] Without significantly deviated points for groups 13, 15, 44, and 80. [d] For alkyl, electronegative, and aryl groups but without group H. [e] Significantly deviated points for groups 10, 12, 13, 15, 38, 44, 80 are excluded. [f] With point for H. [g] Without significantly deviated points for groups 2, 25, 29, 34, 41, 44, and 80. The numeration of groups is in accordance with that used in Appendix I.

Eqns. (4) and (5) to the experimental data indicates[9,16] that the ratio of contributions of different mechanisms in the combined effects measured by scales X_1 and X_2 of group

R_1 and R_2 on $\delta^{13}C$ is constant at first approximation. An analysis of these measures for the most representative set of 47 alkyl, electronegative aliphatic, aryl substituents and H has shown that they, in fact, may be described as a linear combination of the inductive ($a_1\sigma^*$), steric ($a_2 n_H^\alpha$) and resonance ($a_3 n_{Ar}$) effects of these substituents (Table 4):

$$X = a_C + a_1\sigma^* + a_2 n_H^\alpha + a_3 n_{Ar} \qquad (8)$$

Here σ^* is the inductive constant of R, n_H^α is the number of H-atoms attached to the C_{sp3} α-atom in R (n = 0,1,2,3), n_{Ar} = 1, when R = aryl group and zero in all other cases; a_1 and a_2 are the sensitivities of X to the inductive effect of substituent and to its branching, respectively, and a_3 is a resonance contribution of the aryl group to X assumed, in accordance with Ref. 18, to be independent of the nature of the ring substituents. The term $a_2 n_H^\alpha$ in Eq. (8) similar to a hyperconjugation term in the extended Taft equation[19] apparently reflects 1,3-non-bonded (steric) interactions as it was shown[13,20] in the analysis of thermodynamic properties of organic compounds. Regressions corresponding to equation (8) (Regs. N.2 and P.2 in Table 4) have a satisfactory quality for X_1 and X_2 after exclusion of a number of significantly deviated points. The regression accuracy ($s\% = s/\Delta$ where s is the standard of regression and Δ is a range of variation of correlated value) is 3.9 and 5.2% for X_1 and X_2, respectively. All the contributions in the regressions are significant and exclusion of one of them sharply decreases both the correlation coefficient and regression standard. Extension of that equation by the term proportional to steric constants E_s of groups R_1 and R_2 leads to its insignificance. As it is seen from Table 4, Regs. M.2 and O.2 obtained for alkyl and electronegative aliphatic groups are particular cases of more general regressions N.2 and P.2.

Comparing the regressions in Table 4 one can see that

inductive, steric, and resonance contributions in the effects of groups R_I and R_2 on the $\delta^{13}C$ value have opposite directions. These regressions also differ considerably in the absolute value of coefficients a_0+a_2, whereas the absolute values of aryl group resonance contribution are nearly equal. These differences are responsible for the absence of correlation between the effects of R_I and R_2 on the $\delta^{13}C_{sp}$. In other words, the total effects of groups R_I and R_2 on the value of $\delta^{13}C_{sp}$ are different linear combinations of the same more fundamental contributions.It should be especially noted that the regressions for X_2 describe well the point for substituent H, whereas the regressions for X_I fail to do this ($\Delta_H = X_{I\ calc.} - X_{I\ exp.} = 16$ ppm!). Similar deviation of substituent H from general regularities is observed in the constants[20] φ used to describe ΔH_f^o for organic compounds and in steric constants E_s (E_s^o)[21].

Thus in compounds $R_IC{=}CR_2$ the substituents R_I and R_2 affect independently the chemical shift value $\delta^{13}C_{sp}$ and their effects, which are linear combinations of the inductive, steric, and resonance contributions, are satisfactorily described in terms of PPL. The above regression equations may be used to estimate chemical shifts. The analysis of the totalities of more consistent experimental data will undoubtedly allow to refine the mathematical form and the limits of application of the relationships found.

All the regressions have been calculated on computer CDRA-1304, using the program of multiple regression analysis based on Draper and Smith algorythms[22] with some our modifications. The risk level of 5% is used for all statistical tests[23,24].

Appendix I

Measures X_1 and X_2 for Various Substituents [a]

	R	X_1	X_2		R	X_1	X_2
1	H	0	0	32	$H_2C{=}CHCH(OH)$	10.8	2.6
2	Me	7.3	-5.0	33	$PhCH{=}CHCH(OH)$-t	10.9	2.7
3	Et	13.0	-4.7	34	$(EtO)_2CH(OH)$	7.2	1.5
4	Pr	11.6	-3.8	35	$MeCH{=}CHCH(OH)$-t	11.6	2.0
5	Bu	12.0	-3.4	36	$Ph_2CHCH(OH)$	11.4	3.1
6	Am	12.1	-3.4	37	t-Bu	20.1	-5.0
7	Hex	13.2	-1.8	38	Ph_3C	17.6	1.3
8	$C_{10}H_{21}$	12.7	-3.2	39	$Me_2C(OH)$	16.8	-1.8
9	$C_{11}H_{23}$	12.4	-3.9	40	$Et(Me)C(OH)$	15.7	-0.7
10	$HOCH_2CH_2$	8.7	-1.5	41	$Ph(Me)C(OH)$	16.9	-1.0
11	$CCl_2{=}CHOCH_2CH_2$	7.8	-1.1	42	$H_2C{=}CH(Me)C(OH)$	14.6	1.4
12	$ClCH_2$	7.6	3.6	43	Ph_3SiCH_2	-2.6	15.2
13	$BrCH_2$	9.1	5.1	44	Me_2NCH_2	6.8	1.7
14	$PhCH_2$	10.4	-0.8	45	$(CH_2)_5NCH_2$	8.3	2.3
15	$HOCH_2$	11.2	3.1	46	$O(CH_2)_4NCH_2$	8.0	3.0
16	$MeOCH_2$	8.2	3.0	47	$(HC{\equiv}CCH_2)_2NCH_2$	6.8	2.4
17	$CCl_2{=}CHOCH_2$	5.7	5.3	48	$\bar{C}l(CH_2)_5\overset{+}{N}H\ CH_2$	1.6	9.6
18	$PhOCH_2$	6.6	3.2	49	$\bar{C}l(Et)_2\overset{+}{N}H\ CH_2$	1.3	9.3
19	p-MeØOCH_2	7.2	3.0	50	$\bar{I}(CH_2)_5\overset{+}{N}(Me)\ CH_2$	5.3	17.1
20	p-MeØOCH_2	7.4	3.1	51	$(CH_2)_5C(OH)$	15.8	0.2
21	p-FØOCH_2	7.0	3.6	52	$(CH_2)_5C(OCOCH_3)$	11.6	2.3
22	p-BrØOCH_2	6.6	3.8	53	$(CH_2)_4C(OCOCH_3)$	12.3	1.2
23	p-IØOCH_2	6.3	4.1	54	$CH_2{=}CH$	8.1	6.8
24	p-$HC{\equiv}CCH_2O$ØOCH_2	8.0	4.8	55	$MeCH{=}CH$-c	8.3	10.1
25	p-NO_2ØOCH_2	6.4	6.0	56	$MeCH{=}CH$-t	10.5	3.8
26	o-NO_2ØOCH_2	7.1	6.2	57	$EtCH{=}CH$-c	8.4	9.2
27	$EtCH(OH)$	12.9	0.9	58	$EtCH{=}CH$-t	10.5	3.7
28	$PhCH(OH)$	11.6	2.9	59	$PrCH{=}CH$-c	8.5	9.3
29	$HC{\equiv}CCH(OH)$	8.4	0.9	60	$PrCH{=}CH$-t	10.6	3.7
30	$MeCH(OH)$	13.8	0.0	61	$MeOCH{=}CH$-c	6.8	8.6
31	i-$PrCH(OH)$	11.7	1.5	62	$EtOCH{=}CH$-c	6.9	8.4

	R	X_1	X_2		R	X_1	X_2
63	PrOCH=CH-c	6.7	8.1	98	p-F_3CØ	10.1	7.5
64	BuOCH=CH-c	6.8	8.0	99	p-N≡CØ	9.8	9.1
65	i-BuOCH=CH-c	6.8	8.2	100	p-NO_2Ø	9.6	9.7
66	s-BuOCH=CH-c	6.9	8.0	101	m-HC≡CØ	10.5	6.9
67	i-PrOCH=CH-c	6.9	8.2	102	o-,o-,p-Me_3Ø	8.1	11.3
68	t-BuOCH=CH-c	7.0	7.6	103	N=C	-14.8	3.0
69	t-BuOCH=CH-t	8.8	3.5	104	i-PrC(O)	8.9	8.0
70	MeSCH=CH-c	8.3	13.2	105	PhC(O)	8.5	10.2
71	EtSCH=CH-c	8.3	12.9	106	MeOOC	12.8	-3.9
72	EtSCH=CH-t	10.1	5.1	107	EtOOC	3.9	-9.4
73	PrSCH=CH-c	8.3	12.9	108	EtO	17.6	-48.6
74	PrSCH=CH-t	10.1	4.9	109	PhO	12.3	-38.3
75	BuSCH=CH-c	8.3	12.8	110	p-MeOØO	13.5	-39.0
76	i-BuSCH=CH-c	8.3	12.8	111	p-MeØO	12.6	-38.9
77	i-PrSCH=CH-c	8.3	12.7	112	p-ClØO	11.8	-37.9
78	t-BuSCH=CH-c	8.3	12.5	113	p-NO_2ØO	10.6	-36.1
79	t-BuSCH=CH-t	10.1	5.2	114	o-MeØO	12.6	-38.4
80	C_6H_{11}	13.5	2.5	115	EtS	0.8	9.6
81	Ph	11.5	5.1	116	$Ph_2P(O)$	5.9	23.3
82	p-NH_2Ø	12.2	2.8	117	$(Me_2N)_2P(O)$	4.4	19.3
83	p-Me_2NØ	12.5	2.8	118	$(EtO)_2P(O)$	1.9	20.2
84	p-MeOØ	11.5	3.7	119	$Bu_2P(O)$	10.6	21.8
85	p-Me_3CØ	11.6	4.4	120	$Et_2P(O)$	9.2	21.6
86	p-Me_2CHØ	12.0	4.9	121	s-Bu_2P	11.4	20.9
87	p-EtØ	11.9	4.8	122	Ph_2P	10.0	24.3
88	p-MeØ	11.6	4.4	123	$(Me_2N)_2P$	11.7	20.5
89	p-PhOØ	11.1	4.4	124	$(EtO)_2P$	13.0	19.8
90	p-PØ	10.4	4.8	125	$Ph_2N(C≡CH)P$	8.1	24.2
91	p-MeSØ	11.3	5.1	126	$(HC≡C)_2P$	4.2	26.2
92	p-Me_3SiØ	11.6	5.4	127	Me_3Si	17.3	21.7
93	p-CH_2=CHØ	11.4	5.6	128	Et_3Si	14.8	23.6
94	p-ClØ	10.4	6.0	129	Ph_3Si	12.7	25.6
95	p-PhØ	11.4	5.6	130	Cl_3Si	9.5	24.7
96	p-BrØ	10.4	6.2	131	$Ph_2Si(C≡CH)$	11.4	26.0
97	p-HC≡CØ	10.9	6.8	132	$Me_2Si(C≡CH)$	14.4	23.4

	R	X_1	X_2		R	X_1	X_2
133	$(p\text{-Me}\phi)_2Si(C{\equiv}CH)$	12.0	25.7	143	Ph_3Sn	12.6	25.5
134	$(p\text{-MeO}\phi)_2Si(C{\equiv}CH)$	12.2	25.6	144	Ph_3Pb	26.6	26.2
135	Me_3Ge	17.1	20.3	145	$MeOOCC_5H_{10}$	12.4	-3.6
136	Et_3Ge	14.4	21.6	146	$MeOOCC_8H_{16}$	12.6	-3.8
137	Bu_3Ge	14.2	20.9	147	$MeOOCC_9H_{18}$	12.7	-3.8
138	Ph_3Ge	12.9	24.6	148	$HC{\equiv}C$	-3.8	-7.6
139	$Ph_2Ge(C{\equiv}CH)$	10.5	23.9	149	$MeC{\equiv}C$	-3.0	-8.0
140	$(C_6F_5)_2Ge(C{\equiv}CH)$	6.1	25.1	150	$HOCH_2C{\equiv}C$	-4.5	-3.4
141	Et_3Sn	14.8	25.6	151	$Me_2C(OH)C{\equiv}C$	-4.2	-2.7
142	$PhC{\equiv}C$	-3.6	-1.1				

[a] These measures are calculated according to equations (2) and (3). The data used are in Appendix II.

Chemical Shifts (ppm from TMS) for Substituted Acetylenes $R_1C{\equiv}CR_2$

R_1 -	C ≡ C		- R_2	ref.	R_1 -	C ≡ C		- R_2	ref.
H	71.95	71.95	H	a	p-BrØOCH_2	78.56	75.80	H	l
Me	79.26	66.96	H	a	p-IØOCH_2	78.26	76.09	H	l
Et	85.0	67.3	H	b	p-HC≡CCH_2OØOCH_2	79.96	76.80	H	l
Pr	83.6	68.2	H	c	p-NO_2ØOCH_2	78.38	77.96	H	l
Bu	84.0	68.6	H	d	o-NO_2ØOCH_2	79.13	78.19	H	h
Am	84.1	68.6	H	d	EtCH(OH)	84.9	72.9	H	g
Hex	85.2	70.2	H	d	PhCH(OH)	83.6	74.9	H	g
$C_{10}H_{21}$	84.7	68.8	H	e	HC≡CCH(OH)	80.4	72.9	H	g
$C_{11}H_{23}$	84.4	68.1	H	f	MeCH(OH)	85.8	72.0	H	g
$HOCH_2CH_2$	80.7	70.5	H	g	i-PrCH(OH)	83.7	73.5	H	g
CCl_2=$CHOCH_2CH_2$	79.79	70.92	H	h	H_2C=CHCH(OH)	82.8	74.6	H	g
$ClCH_2$	79.6	75.6	H	i	PhCH=CHCH(OH)-t	82.9	74.7	H	g
$BrCH_2$	81.1	77.1	H	i	$(EtO)_2CH$	79.2	73.5	H	g
$PhCH_2$	82.41	71.24	H	j	MeCH=CHCH(OH)-t	83.6	74.0	H	g
$HOCH_2$	83.2	75.1	H	i	$Ph_2CHCH(OH)$	83.4	75.1	H	g
$MeOCH_2$	80.20	75.00	H	k	t-Bu	92.14	67.00	H	m
CCl_2=$CHOCH_2$	77.67	77.29	H	h	Ph_3C	89.56	73.30	H	j
$PhOCH_2$	78.63	75.17	H	l	$Me_2C(OH)$	88.8	70.2	H	g
p-MeOØOCH_2	79.25	75.04	H	l	Bt(Me)C(OH)	87.7	71.3	H	g
p-MeØOCH_2	79.44	75.12	H	l	Ph(Me)C(OH)	87.2	73.1	H	g
p-FØOCH_2	79.02	75.62	H	l	H_2C=CH(Me)C(OH)	86.6	73.4	H	n

R_1 -	C	C	- R_2	ref	R_1 -	C	C	- R_2	ref
Ph_3SiCH_2	69.42	87.16	H	j	i-PrOCH=CH-c	78.94	80.16	H	q
Me_2NCH_2	78.85	73.66	H	k	t-BuOCH=CH-c	79.03	79.65	H	q
$(CH_2)_5NCH_2$	80.3	74.3	H	n	t-BuOCH=CH-t	80.83	75.46	H	q
$O(CH_2)_4NCH_2$	80.0	75.0	H	n	MeSCH=CH-c	80.32	85.25	H	q
$(HC{\equiv}CCH_2)_2NCH_2$	78.8	74.4	H	n	BtSCH=CH-c	80.29	84.92	H	q
$Cl^-(CH_2)_5\overset{+}{N}HCH_2$	73.6	81.6	H	n	EtSCH=CH-t	82.11	77.12	H	q
$Cl^-(C_2H_5)_2\overset{+}{N}HCH_2$	73.3	81.3	H	n	PrSCH=CH-c	80.29	84.92	H	q
$I^-(CH_2)_5\overset{+}{N}(Me)CH_2$	77.3	89.1	H	n	PrSCH=CH-t	82.06	76.91	H	q
$(CH_2)_5C(OH)$	87.8	72.2	H	g	BuSCH=CH-c	80.30	84.80	H	q
$(Ch_2)_4C(OCOMe)$	84.3	73.2	H	g	i-BuSCH=CH-c	80.28	84.85	H	q
$(CH_2)_5C(OCOMe)$	83.6	74.3	H	g	t-BuSCH=CH-c	80.32	84.50	H	q
CH_2=CH	80.1	78.8	H		i-PrSCH=CH-c	80.28	84.72	H	q
MeCH=CH-c	80.3	82.1	H	p	t-BuSCH=CH-t	82.06	77.22	H	q
MeCH=CH-t	82.5	75.8	H	p	ClCH=CH-c	87.5	78.1	H	o
EtCH=CH-c	80.4	81.2	H	p	ClCH=CH-t	82.1	79.2	H	o
EtCH=CH-t	82.5	75.7	H	p	C_6H_{12}	85.5	74.5	H	p
PrCH=CH-c	80.5	81.3	H	p	Ph	83.52	77.06	H	r
PrCH=CH-t	82.6	75.7	H	p	p-NH_2Ø	84.20	74.77	H	r
MeOCH=CH-c	78.81	80.58	H	q	p-N(Me)$_2$Ø	84.52	74.78	H	r
EtOCH=CH-c	78.88	80.35	H	q	p-MeOØ	83.52	75.67	H	r
PrOCH=CH-c	78.74	80.10	H	q	p-Me_3CØ	83.62	76.36	H	r
BuOCH=CH-c	78.81	80.03	H	q	p-Me_2CHØ	84.0	76.9	H	s
i-BuOCH=CH-c	78.85	80.15	H	q	p-EtØ	83.9	76.8	H	s

R_1 -	C	C	- R_2	ref	R_1 -	C	C	- R_2	ref
p-MeØ	83.62	76.36	H	r	PhO	84.34	33.64	H	x
p-PhOØ	83.12	76.41	H	r	p-MeOØO	85.46	33.00	H	x
p-FØ	82.43	76.82	H	r	p-MeØO	84.61	33.09	H	x
p-MeSØ	83.28	77.07	H	r	p-ClØO	83.78	34.10	H	x
p-Me_3SiØ	83.63	77.37	H	r	p-NO_2ØO	82.64	35.93	H	x
p-CH_2=CHØ	83.43	77.62	H	r	o-MeØO	84.62	33.60	H	x
p-ClØ	82.36	78.03	H	r	EtS	72.8	81.6	H	u
p-PhØ	83.43	77.62	H	r	$Ph_2P(O)$	77.9	95.3	H	y
p-ErØ	82.38	78.21	H	r	$(Me_2N)_2P(O)$	76.4	91.3	H	y
p-HC≡CØ	82.92	78.83	H	r	$(EtO)_2P(O)$	73.9	92.2	H	y
p-P_3CØ	82.08	79.49	H	r	$Bu_2P(O)$	82.6	93.8	H	u
p-N≡CØ	81.83	81.08	H	r	$Et_2P(O)$	81.2	93.6	H	u
p-NO_2Ø	81.59	81.74	H	r	e-Bu_2P	83.4	92.9	H	u
m-HC≡CØ	82.5	78.9	H	t	Ph_2P	82.0	96.3	H	y
o-,o-,p-Me_3Ø	80.1	83.3	H	u	$(Me_2N)_2P$	83.7	92.5	H	y
N≡C	57.16	74.98	H	h	$(EtO)_2P$	85.0	91.8	H	y
i-PrC(O)	80.87	80.00	H	v	$Ph_2NP(C≡CH)$	80.1	96.2	H	y
PhC(O)	80.52	82.16	H	v	$(HC≡C)_2P$	76.2	98.2	H	u
MeOOC	84.75	68.10	H	w	Me_3Si	89.28	93.71	H	m
EtOOC	75.09	75.38	H	h	Et_3Si	86.77	95.59	H	m
MeOOCC_5H_{10}	84.35	68.40	H	w	Ph_3Si	85.47	98.46	H	j
MeOOCC_7H_{14}	84.60	68.25	H	w	Cl_3Si	81.46	96.66	H	h
EtO	89.6	23.4	H	u	$Ph_2Si(C≡CH)$	83.45	98.01	H	j

R_1 -	C ≡ C		- R_2	ref	R_1 -	C ≡ C		- R_2	ref
$(p\text{-}MePh)_2Si(C{\equiv}CH)$	83.97	97.68	H	j	Me	75.2	79.3	$C_{10}H_{21}$	f
$(p\text{-}MeOPh)_2Si(C{\equiv}CH)$	84.17	97.55	H	j	Et	80.5	80.5	Et	aa
$Me_2Si(C{\equiv}CH)$	86.38	95.41	H	j	Et	81.3	78.9	Pr	aa
Me_3Ge	89.13	92.27	H	m	Et	80.3	84.9	i-Pr	aa
Et_3Ge	86.39	93.60	H	m	Et	82.2	80.9	Bu	c
Bu_3Ge	86.2	92.9	H	u	Et	82.0	78.0	s-Bu	aa
Ph_3Ge	84.88	96.64	H	j	Et	79.6	87.8	t-Bu	aa
$Ph_2Ge(C{\equiv}CH)$	82.48	95.93	H	j	Et	82.6	77.4	i-Bu	aa
$(C_6F_5)_2Ge(C{\equiv}CH)$	78.06	97.10	H	j	Et	79.9	81.7	C_8H_{17}	e
Me_3Sn	89.25	97.30	H	bb	Et	79.5	81.5	C_9H_{19}	f
Et_3Sn	86.75	97.58	H	m	Pr	80.2	80.2	Pr	e
Ph_3Sn	84.60	97.54	H	z	Pr	80.0	80.0	Hep	e
Ph_3Pb	98.61	98.21	H	z	Pr	79.9	80.2	C_8H_{17}	f
$MeOOCC_8H_{16}$	84.70	68.15	H	w	i-Pr	84.6	84.6	i-Pr	aa
Me	73.9	73.9	Me	b	i-Pr	84.0	87.6	t-Bu	aa
Me	74.2	80.3	Et	aa	Bu	80.0	80.0	Hex	e
Me	74.9	78.7	Pr	aa	Bu	80.0	80.0	Hep	f
Me	74.1	84.6	i-Pr	aa	t-Bu	86.8	86.8	t-Bu	aa
Me	75.4	78.8	Bu	e	Am	80.5	80.5	Am	e
Me	75.6	77.8	s-Bu	aa	Am	80.1	80.1	Hex	f
Me	73.3	87.6	t-Bu	aa	Me	81.6	77.7	CH_2OH	g
Me	76.0	79.7	Am	e	Me	77.9	84.4	$C(OH)Me_2$	g
Me	75.3	79.1	C_9H_{19}	e	Me	86.4	80.4	Ph	cc

R_1	- C ≡ C -	R_2	ref
Me	84.7	80.2	ØOMe-p	cc
Me	85.6	80.8	ØMe-p	cc
Me	87.7	79.6	ØCl-p	cc
Me	88.2	79.4	ØCl-m	cc
Me	28.2	88.6	OMe	u
Me	105.8	75.2	$P(O)Cl_2$	y
Me	105.2	74.3	$P(O)Ph_2$	y
Me	98.4	72.8	$P(O)(NMe_2)_2$	y
Me	98.1	71.2	$P(O)(OBt)_2$	y
Me	101.3	75.4	$P(O)(C{\equiv}CMe)_2$	y
Me	105.7	75.5	PPh_2	y
Me	101.4	78.7	$P(NMe_2)_2$	y
Me	102.8	71.3	$P(C{\equiv}CMe)_2$	y
Me	101.6	80.8	$P(OEt)_2$	y
Me	100.69	82.72	$GeMe_3$	h
Me	102.29	79.77	$GeEt_3$	h
Me	105.76	81.55	$SnMe_3$	bb
Me	75.40	79.30	$C_7H_{14}COOMe$	w
Et	35.7	87.8	OEt	u
Et	92.4	67.0	SMe	u
Et	112.37	81.32	$SnMe_3$	bb
Et	81.80	79.40	$C_6H_{12}COOMe$	w
Pr	80.35	80.00	$C_5H_{10}COOMe$	w
Pr	94.81	80.43	$COØ(OMe)_2$-m,-p	h
Bu	80.75	79.45	C_4H_8COOMe	w
Bu	68.8	56.7	Cl	dd
Bu	79.8	38.4	Br	dd
Bu	96.8	-3.3	I	dd
Bu	92.0	83.1	Ph	dd
Bu	79.0	68.3	C≡CBu	dd
Bu	91.15	81.55	C(O)Me	v
Bu	92.11	81.18	C(O)Pr	v
Bu	91.78	81.49	C(O)Bu-i	v
Bu	93.12	80.13	C(O)Pr-i	v
Bu	95.42	80.01	C(O)Ph	v
Bu	108.34	81.14	$SiEt_3$	m
Bu	110.4	81.4	$SnMe_3$	bb
Bu	111.38	79.73	$SnEt_3$	m
Am	81.40	78.75	C_3H_6COOMe	w
Hex	81.25	78.10	C_2H_4COOMe	w
Hex	107.31	80.37	$GeEt_3$	m
Hex	111.48	76.80	$GeCl_3$	h
Hex	111.47	79.79	$SnEt_3$	m
Hep	84.00	71.35	CH_2COOMe	w
C_8H_{17}	90.00	72.95	COOMe	w
$HOCH_2$	83.7	83.7	CH_2OH	g

R_1 - C ≡ C - R_2				ref
$HOCH_2$	86.9	82.4	CH_2OMe	n
$HOCH_2$	86.3	82.0	CH_2Cl	n
$HOCH_2$	78.2	45.7	Er	g
$HOCH_2CH_2$	103.9	84.0	$SiMe_3$	g
$HOCH_2$	86.7	81.6	CH_2NMe_2	n
$HOCH_2$	86.3	79.0	CH_2NEt_2	n
$HOCH_2$	92.9	75.6	$CH_2\overset{+}{N}Me_3\bar{I}$	n
$HOCH_2$	92.2	75.1	$CH_2\overset{+}{N}(Me)Et_2\bar{I}$	n
$HOCH_2$	92.2	74.6	$CH_2\overset{+}{N}(CH_2)_5(Me)\bar{I}$	n
HOCH(Ph)	91.8	76.5	$CH_2\overset{+}{N}HEt_2\bar{Cl}$	n
MeCH(OH)	85.6	85.6	CH(OH)Me	g
$Me_2C(OH)$	43.3	91.3	OEt	g
$Me_2C(OH)$	96.5	82.6	$CH=CH_2$	n
$Me_2C(OH)$	97.62	76.27	CH=CHOMe-c	h
$Me_2C(OH)$	102.39	78.15	CH=CHSMe-c	h
$Me_2C(OH)$	97.33	77.23	$CH=CHOCMe_3$-c	h
$Me_2C(OH)$	102.31	78.83	$CH=CHSCMe_3$-c	h
$Me_2C(OH)$	89.69	56.09	C≡N	h
$Me_2C(OH)$	97.2	82.6	C(O)Me	n
$Me_2C(OH)$	100.9	81.6	C(O)Ph	n
$Me_2C(OH)$	84.3	65.1	$C\equiv CC(OH)Me_2$	n
$Me_2C(OH)$	85.7	43.8	Er	n
PhCH(OH)	88.3	81.0	CH_2NEt_2	n

R_1 - C ≡ C - R_2				ref
Ph(Me)C(OH)	84.9	46.5	Er	n
$CH_2=CHCMe(OH)$	82.4	44.6	Er	n
$(CH_2)_5C(OH)$	91.6	79.0	CH_2NMe_2	n
$(CH_2)_5C(OH)$	94.2	74.6	$CH_2(\overset{+}{H}NMe_2)\bar{Cl}$	n
$(CH_2)_5C(OH)$	96.9	74.0	$CH_2\overset{+}{N}Me_3\bar{I}$	n
$HOCH_2$	104.84	89.21	$SiMe_3$	h
$MeOCH_2$	102.88	87.78	$GeEt_3$	m
$MeOCH_2$	106.71	87.89	$SnEt_3$	m
$ClCH_2$	104.75	89.84	$SnEt_3$	m
$ErCH_2$	104.82	90.66	$SnEt_3$	m
$ClCH_2$	103.80	91.20	$SnMe_3$	bb
$ErCH_2$	103.82	91.65	$SnMe_3$	bb
Et_2NCH_2	101.12	85.00	$GeEt_3$	ee
$O(CH_2)_4NCH_2$	99.11	82.32	$GeEt_3$	ee
$(CH_2)_5NCH_2$	101.88	84.95	$GeEt_3$	ee
Et_2HCH_2	104.84	86.78	$SnMe_3$	bb
$EtOCH_2$	106.28	88.80	$SnMe_3$	bb
$EtSCH_2$	105.62	83.80	$SnMe_3$	bb
Et_2NCH_2	105.04	87.27	$SnEt_3$	h
$O(CH_2)_4NCH_2$	102.24	86.55	$SnEt_3$	h
$CH_2=CH$	91.38	82.20	SMe	ff
$CH_2=CH$	92.94	80.45	SEt	ff
$CH_2=CH$	92.26	80.84	SPr	ff

R_1 -	C	C	- R_2	ref	R_1 -	C	C	- R_2	ref
CH_2=CH	92.35	80.95	SBu	ff	Ph	107.32	47.95	TeØF-p	h
CH_2=CH	97.35	72.57	SeMe	ff	Ph	106.94	91.22	$SiEt_3$	m
CH_2=CH	98.82	71.19	SeEt	ff	Ph	106.46	91.03	$GeEt_3$	m
CH_2=CH	98.84	71.67	SePr	ff	Ph	110.57	91.73	$SnEt_3$	m
CH_2=CH	109.66	49.48	TeMe	ff	Ph	107.62	84.38	$GeCl_3$	h
CH_2=CH	110.78	46.14	TeEt	ff	Ph	89.67	88.70	C(O)Me	v
CH_2=CH	105.24	92.04	$SiEt_3$	m	Ph	90.09	88.06	C(O)Et	v
CH_2=CH	104.66	92.14	$GeEt_3$	m	Ph	89.81	88.28	C(O)Pr	v
CH_2=CH	109.07	92.68	$SnEt_3$	m	Ph	90.93	87.20	C(O)Pr-i	v
MeCH=CH-c	103.0	100.0	$SiMe_3$	p	Ph	91.66	87.15	C(O)Ph	v
MeCH=CH-t	104.0	92.2	$SiMe_3$	p	Ph	90.62	87.50	C(O)ØOMe-p	v
EtCH=CH-c	101.9	99.4	$SiMe_3$	p	Ph	92.54	87.02	C(O)ØBr-p	v
EtCH=CH-t	104.2	92.4	$SiMe_3$	p	Ph	96.07	86.22	C(O)ØOH-o	h
PrCH=CH-c	102.2	98.3	$SiMe_3$	p	Ph	90.68	89.85	C(O)C≡CPh	h
PrCH=CH-t	104.2	92.4	$SiMe_3$	p	Ph	91.35	87.46	$C(O)Ø(OMe)_2$-m,-p	h
CH_2=CH	69.2	68.6	Cl	o	p-MeOØ	92.94	86.86	C(O)Ph	v
Ph	98.33	72.36	SeMe	h	p-MeØ	92.22	87.03	C(O)Ph	v
Ph	103.09	70.09	SePh	h	p-BrØ	89.98	88.08	C(O)Ph	v
Ph	102.87	71.04	SeØMe-p	h	p-NO_2Ø	89.47	89.24	C(O)Ph	v
Ph	103.90	69.44	SeØBr-p	h	p-MeOØ	92.88	86.49	C(O)ØOMe-p	h
Ph	103.57	69.75	SeØCl-p	h	p-BrØ	90.30	88.40	C(O)ØOMe-p	h
Ph	109.50	46.80	TeØMe-p	h	p-MeOØ	92.23	86.10	$C(O)Ø(OMe)_2$-m,-p	h
Ph	108.06	46.96	TeØCl-p	h	PhC(O)	86.06	86.06	C(O)Ph	h

R_1 - C ≡ C - R_2				ref	R_1 - C ≡ C - R_2				ref
Me_3Si	86.89	108.81	CH(OH)Me	h	MeTe	66.32	66,32	TeMe	ii
Me_3Si	96.13	94.56	COOH	gg	MeSe	79.16	79.16	SeMe	ii
Me_3Si	101.34	102.59	C(O)H	gg	$(EtO)_2P(O)$	78.89	97.69	ØP-p	k
Me_3Si	95.43	102.86	C(O)Me	gg	$(EtO)_2P(O)$	79.20	99.47	Ph	k
Me_3Si	102.07	96.63	C(O)Cl	gg	$(EtO)_2P(O)$	77.98	99.36	ØMe-p	k
Me_3Si	99.18	101.23	C(O)Ph	gg	$(EtO)_2P(O)$	79.62	97.39	ØCl-p	k
Me_3Si	97.70	100.12	$C(O)CH=CH_2$	gg	$(EtO)_2P(O)$	77.32	99.66	ØOMe-p	k
Me_3Si	91.97	95.63	COOEt	gg	H≡C	63.17	83.20	Ph	h
Me_3Si	36.68	109.46	OEt	h	$(EtO)_2P(O)$	96.58	115.21	$SnMe_3$	bb
Me_3Si	110.61	114.94	$SiEt_3$	h	$SnEt_3$	114.41	114.41	$SnEt_3$	h
Me_3Si	113.02	113.02	$SiMe_3$	h	Me_3Sn	112.11	114.37	$GeEt_3$	bb
Et_3Si	112.36	112.36	$SiEt_3$	h	Me_3Sn	114.40	115.08	$SiEt_3$	bb
Et_3Si	98.08	96.09	SEt	h	Me_3Sn	115.36	115.36	$SnMe_3$	bb
Me_3Ge	35.93	108.20	OEt	h	Me_3Sn	110.55	117.29	$GeMe_3$	bb
Me_3Ge	108.66	114.84	$SiEt_3$	h	Me_3Sn	113.03	117.78	$SiMe_3$	bb
Et_3Ge	97.71	94.13	SEt	h	Me_3Sn	79.56	119.60	Eu-t	bb
Et_3Ge	110.02	110.02	$GeEt_3$	h	Me_3Sn	80.80	108.68	CH_2SiMe_3	bb
Et_3Ge	109.96	114.39	$SnEt_3$	h	Me_3Sn	94.64	94.44	OP_3	bb
Et_3Sn	31.67	113.29	OEt	h	Me_3Sn	98.77	79.35	C≡N	bb
Et_3Sn	98.41	97.64	SEt	h	Me_3Sn	73.46	80.20	Cl	bb
MeS	99.03	97.93	$SnMe_3$	bb	Me_3Sn	85.24	61.68	Br	bb
MeS	84.78	84.78	SMe	ii	Me_3Sn	33.03	115.07	OMe	bb

R_1 -	C ≡ C		- R_2	ref
Me_3Sn	33.98	112.50	OBt	bb
Me_3Sn	97.28	99.49	SBt	bb
Me_3Sn	110.04	91.13	C_6F_5	bb
HC≡C	68.21	64.45	H	kk
HeC≡C	69.03	63.97	H	kk
EtC≡C	69.00	68.14	H	ii
BuC≡C	68.91	64.49	H	h
t-BuC≡C	68.72	65.67	H	h
$HOCH_2C≡C$	67.5	68.6	H	ll
$(CH_2)_5HCH_2C≡C$	68.28	66.83	H	h
$Me_2C(OH)C≡C$	67.81	69.29	H	kk
PhC≡C	68.35	70.90	H	kk
Me	73.60	64.74	C≡CH	kk
Et	78.50	65.40	C≡CH	ii
Bu	78.10	65.34	C≡CH	h
t-Bu	85.01	64.21	C≡CH	h
$HOCH_2$	74.7	69.7	C≡CH	ll
$(CH_2)_5HCH_2$	73.28	69.51	C≡CH	h
$Me_2C(OH)$	81.05	66.70	C≡CH	kk
Ph	75.06	74.03	C≡CH	kk
Me	72.0	64.8	C≡CMe	ll
Et	78.5	65.4	C≡CEt	ll
$HOCH_2$	77.9	69.3	$C≡CCH_2OH$	ll

R_1 -	O ≡ O		- R_2	ref
MeCH(OH)	81.3	67.8	C≡CCH(OH)Me	ll
$Me_2C(OH)$	84.1	74.0	$C≡CC(OH)Me_2$	ll
Ph	81.7	74.0	C≡CPh	ll
MeC≡C	67.48	79.79	$C(OH)Me_2$	kk
MeC≡C	60.0	60.0	C≡CMe	mm
MeC≡C	89.2	82.7	$SiMe_3$	e
BtC≡C	78.73	68.14	SMe	ii
BtC≡C	84.43	59.58	SeMe	ii
EtC≡C	95.79	34.59	TeMe	ii
PrC≡C	70.5	73.8	CH_2OH	ll
PrC≡C	68.9	77.4	CH(OH)Me	ll
PrC≡C	86.7	71.0	CH=CHCOOMe	mm
$HOCH_2C≡C$	70.2	80.8	Ph	ll
$MeCOOCH_2CH_2$	73.6	66.5	$C≡CCH_2CH_2OOCMe$	em
$MeCOOCH_2$	73.9	69.8	CH_2COOMe	mm
PhCH(OH)	79.7	69.9	CH(OH)Ph	ll
Et(Me)C(OH)	82.9	68.9	C(OH)(Me)Bt	ll
$Me_2C(OH)C≡C$	74.57	79.11	Ph	kk
t-BuC≡C	62.3	61.9	$(C≡C)_3Bu-t$	mm
Me_3Si	84.0	88.7	$C≡CSiMe_3$	c
Me	76.94	64.34	$C≡CC(OH)Me_2$	kk
Me	74.8	65.0	$(C≡C)_2Me$	mm
Me	76.0	65.4	$C≡CSiMe_3$	c

R_1 -	C ≡ C		- R_2	ref	R_1 -	C ≡ C		- R_2	ref
Et	83.60	65.22	C≡CSMe	ii	MeOOC	73.50	87.95	$CH_2CH_2C{\equiv}CC_{11}H_{23}$	w
Et	82.40	65.33	C≡CSeMe	ii	$MeOOCCH_2$	72.30	82.45	$CH_2CH_2C{\equiv}CC_{10}H_{21}$	w
Et	82.57	65.66	C≡CTeMe	ii	$MeOOC(CH_2)_2$	79.05	79.80	$CH_2CH_2C{\equiv}CC_9H_{19}$	w
Pr	81.5	64.7	$C{\equiv}CCH_2OH$	ll	$MeOOC(CH_2)_3$	79.80	79.95	$CH_2CH_2C{\equiv}CC_8H_{17}$	w
Pr	81.4	64.7	C≡CCH(OH)Me	ll	$MeOOC(CH_2)_4$	80.40	79.35	$CH_2CH_2C{\equiv}C$Hep	w
Pr	90.0	65.3	C≡CCH=CHCOOMe	mm	$MeOOC(CH_2)_5$	80.80	79.15	$CH_2CH_2C{\equiv}C$Hex	w
$HOCH_2$	78.3	73.5	C≡CPh	ll	$MeOOC(CH_2)_6$	80.95	79.00	$CH_2CH_2C{\equiv}C$Am	w
$Me_2C(OH)$	87.91	67.87	C≡CPh	kk	$MeOOC(CH_2)_7$	81.10	78.95	$CH_2CH_2C{\equiv}C$Bu	w
t-Bu	88.5	64.6	$(C{\equiv}C)_4$Bu-t	mm	$MeOOC(CH_2)_8$	81.10	78.90	$CH_2CH_2C{\equiv}C$Pr	w
t-Bu$(C{\equiv}C)_2$	61.8	61.8	$(C{\equiv}C)_2$Bu-t	mm	$MeOOC(CH_2)_9$	81.15	78.85	$CH_2CH_2C{\equiv}C$Bt	w
$(CH_2)_5C(OH)$	83.1	68.2	$C{\equiv}CC(OH)(CH_2)_5$	ll	$MeOOC(CH_2)_{10}$	81.25	78.80	$CH_2CH_2C{\equiv}C$Me	w
MeOOC	80.50	74.60	$CH_2C{\equiv}CCOOMe$	w	$C_{11}H_{23}$	81.45	78.50	$CH_2CH_2C{\equiv}CCH_2COOMe$	w
MeOOC	81.20	78.80	$CH_2CH_2C{\equiv}CCOOMe$	w	$MeOOC(CH_2)_{11}$	81.65	78.15	$CH_2CH_2C{\equiv}CH$	w
$MeOOC(CH_2)_5$	80.10	74.90	$CH_2C{\equiv}C$Am	w	Am	80.60	74.50	$CH_2C{\equiv}C(CH_2)_5COOMe$	w

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